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NUMBER 2



April, 1946

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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OXIDATIVE BREAKDOWN OF RUBBER *

E. H. FARMER

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS, ENGLAND

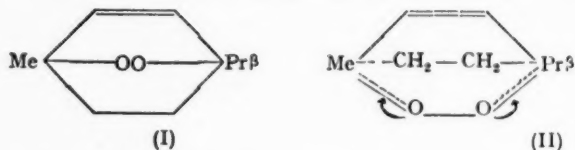
Scope of Survey.—The autooxidation of vegetable and animal drying oils causes solidification, hardening, and toughening of the original olefinic material, whereas absorption of oxygen by natural rubber normally causes softening, with loss of strength and elasticity. Various synthetic rubbers appear to take an intermediate position between drying oils and natural rubber, but with none of the rubbers does autooxidation represent a simple phenomenon, leading uniformly to softening as opposed to toughening. The peroxidation process which forms the basis of autooxidation leads in general to two opposite effects, *viz.*, to oxidative chain-scission (degradation) and to molecule-linking (polymerization or oxygen-vulcanization), and it seems logical to associate the former with the softening of olefinic materials and the latter with their toughening or oxygen-vulcanization. What, however, is far from clear is the cause of onset under given conditions of softening on the one hand or oxygen-vulcanization on the other, and the precise nature of the molecular changes which underlie the two phenomena. At present even qualitative information concerning the intricate course of autooxidative reactions among olefinic substances is far from abundant, and the necessary kinetic evidence which must both set the final seal of credibility on those chemical explanations which careful experimentation indicates to be sound, and in difficult cases discriminate between alternative possible explanations, is only beginning to become available. The most useful contribution, therefore, which can be made at the moment is to clarify in terms of organic structure and reactions the basic issues involved, and to show how far existing chemical information provides certain or possible explanations of the broad lines of autooxidative molecular breakdown (and its converse) as it is encountered among rubbers.

Peroxidation the Prerequisite of Autooxidative Molecular Change.—There is ever-growing evidence to show that molecules of oxygen which are absorbed by olefinic substances are incorporated as a whole to form organic peroxides or peroxido radicals. These peroxidic products may be so unstable as to have only a brief existence under the reaction conditions employed, in which case they are represented in the reaction mixture by their secondary (decomposition or transformation) products or, alternatively, they may be composed of molecules possessing considerable inherent stability, in which case they survive in large measure to the end of the oxidation process and well beyond. Where the stability of the peroxido groups is high the introduction of the latter must, of course, have a direct and specific effect (more or less permanent, and generally speaking, tending towards hardening) on the physical properties of the autooxidized material; but where it is low, as happens generally with the various rubbers, the really important feature in relation to the quality, or physical properties of the autooxidized material, is not so much the introduction of the groups (although the number of these is connected with the degree of autooxida-

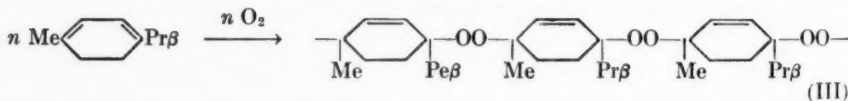
* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 2, pages 122-132, August 1945.

tive change), as the manner of their decomposition. The decomposition of peroxides may in general be envisaged as arising from thermal, photochemical or from chemical causes, and although short-wave light is possibly an important degradative influence in certain circumstances, the most usual mode of peroxide breakdown encountered in the normal (nonchemical) manipulation of rubbers is likely to be the thermally promoted type. Therefore to be able to account for the changes in the properties of autooxidized rubber it is necessary to understand the courses of thermal breakdown of peroxides of appropriate types. Unfortunately knowledge of the fate of peroxides and of the use that is made of the chemical energy of which they are rich repositories must be based on studies of isolable (and therefore relatively stable) compounds, and deductions derived from these favorable cases applied to the more ephemeral examples. Consideration of the autooxidation process is made easier if the more important characteristics of peroxides known to be formed by the action of oxygen on olefinic substances are reviewed.

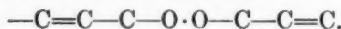
Peroxide Types.—The most stable peroxide type is that represented by ascaridol, a cyclic peroxide (I) which occurs naturally in *Chenopodium* oil. This compound is sufficiently stable both to permit of its rectification at 10–15 mm. pressure, and to resist anything like complete reaction by reducing agents ordinarily used in the determination of peroxides. The high stability probably depends on the possession of a semiaromatic constitution to be represented by (II).



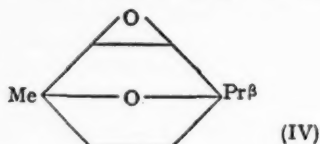
If the artificial preparation of this peroxide be attempted by reacting on the corresponding conjugated hydrocarbon diene (α -terpinene) with oxygen, there results a low molecular polymeric peroxide which is doubtless a polymer mixture containing but little monomer. This polymeric peroxide is almost certainly constituted in the main as in (III), the free ends of the dimer, trimer, etc., chains being joined to form ringed structures¹, or more probably stabilized either by formation of terminal hydroperoxide groups or by disproportionation.



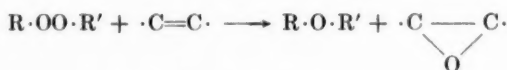
The observed high degree of thermal stability at temperatures below 100° probably arises from the presence of a semiconjugated chain



When the monomeric peroxide (I) is heated in inert solvents to 150° it decomposes fairly smoothly, without explosion, to give the dioxide (IV)².

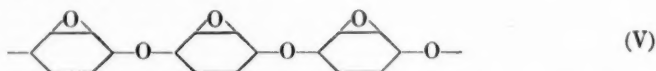


Exactly how the transformation from peroxide to oxide occurs, and especially whether it occurs by intramolecular means is still unknown. The most usual path of thermal decomposition of peroxide groups appears to involve scission between the peroxidic oxygen atoms (as also is the case with catalytic hydrogenation and chemical reduction processes), but whether the diradical which would be formed by such interoxygen scission occurring in (I) could yield (IV) by arrangement is somewhat uncertain; on the other hand bimolecular reaction of the type:

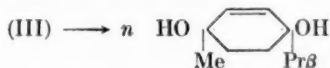


seems doubtful in view of the fact that the heating together of ascaridol and cyclohexene at 150° has not been found to yield recognizable amounts of cyclohexene oxide³.

There is little evidence available as to the detailed way in which the polymeric peroxides decompose thermally. Like most organic peroxides the polymers explode when heated above 130°, but under suitable conditions of dilution they can be decomposed quietly by thermal or reductive treatment. Much information regarding constitution can be derived by their reduction—especially reduction by catalytic hydrogenation, but even under the mild conditions of catalytic hydrogenation the peroxide does not usually escape some considerable measure of catalyzed nonreductive breakdown or of a redistribution of peroxidic oxygen, which has been termed by Bodendorf isomerization. Probably these side reactions are greatly accelerated by metallic surfaces or by reagent ions⁴, but it is unlikely that this so-called isomerization involves smooth oxygen redistribution without the occurrence of some degree of oxidative scission. It may be noted that the strict polymeric analog of the change I → IV would yield polyether—polyoxide chains:



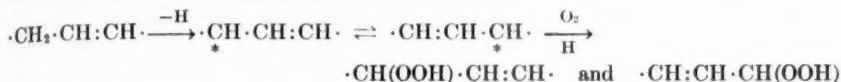
Experiment shows that the three cyclic conjugated dienes, α -terpinene, α -phellandrene and cyclohexadiene, all behave alike in giving low-molecular polymeric peroxides on oxidation, and these latter in accordance with a constitution of the type shown in (III) give on catalytic hydrogenation considerable yields of the expected dihydroxylated monomers¹:



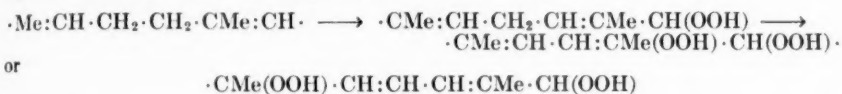
but no smooth transformation of the type III → V has ever yet been recognized.

In passing from cyclic to open-chain diolefinic substances of conjugated structure, a variant of the above-described behavior is encountered. The peroxides formed by autooxidation are again mainly of stable polymeric 1,4-type, doubtless containing the basic chain $(\cdot C : C : C : C \cdot OO \cdot)_n$ with joined or otherwise stabilized ends, but a proportion of them (up to 20 per cent) undergoes oxidative scission—scission which may occur wholly spontaneously and unavoidably during the absorption of oxygen, or otherwise may (apparently) first occur in the presence of metallic catalysts during attempted hydrogenation of the peroxides. Sorbic ester, $CH_2 : CH : CH : CH : CH : CO_2Me$, α, δ -diphenylbutadiene $CHPh : CH : CH : CHPh$, are examples of the spontaneous

isomerism but not conjugation:



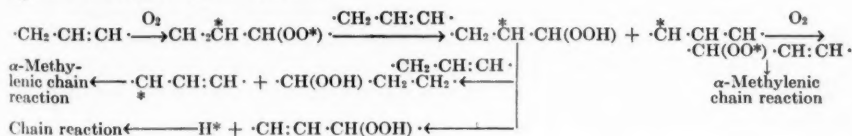
These simple systems are interesting in view of their relation to, but differentiation from, those occurring in natural and in polybutadiene synthetic rubbers, for in these materials the double bonds are separated from one another by pairs of methylene groups. Absorption of oxygen leads to hydroperoxidation but any effective movement towards the production of conjugated peroxides would necessitate two successive double bond shifts, which could only be promoted by successive attacks by oxygen at the same methylenic pair:



In practice, conjugation is not realized to any appreciable extent, any more than is the corresponding isomerization of natural rubber to conjugated forms by the action of boiling, strong alkali, although it can occur extensively with the systems:

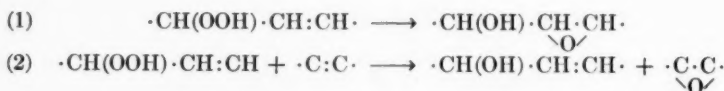


The Initiation of Oxidative Attack.—Three facts stand out in connection with the problem of how oxidative attack is initiated in monoolefinic and rubberlike systems. The first of these is that any detachment of an α -methylenic hydrogen atom to leave an active 3-carbon radical, $\cdot\text{CH}:\text{CH}:\text{CH}\cdot$, requires the expenditure of 80 k.cal. of energy, which must be supplied from some source; the second is that peroxidation, whether photochemically or thermally promoted, is substantially independent of pressure and is autocatalytic; and the third is that experiment shows that in conjugated compounds, even those in which the diene or polymer systems are flanked by α -methylene groups, *e.g.*, sorbic and elaeostearic esters, peroxidation affects only the double bonds, thus leaving the β -methylene groups intact. Since, therefore, it is clear: (1) that molecular oxygen is intrinsically quite able to begin its attack at a double bond, presumably by adding at one end of it; (2) that the monomeric peroxides of simple olefins and of unconjugated polyolefins are undoubtedly α -methylenic hydroperoxides; (3) that the above-mentioned very high expenditure of energy at the outset of reaction, which is essential if the first step is deemed to be the radical dissociation of C—H, is greatly diminished if the oxygen begins its attack in some few of the olefin molecules by adding at double bonds and thereafter continues the attack by means of chain reactions, and (4) that the oxidation has none of the features of ionic reactivity, it then appears most sound and reasonable to postulate tentatively universal initiation of autooxidative attack in all kinds of olefinic systems by additive reaction occurring at double bond centers, and to formulate the α -methylenic reaction for unconjugated olefins by the intermolecular scheme:



In this way the extent of actual addition at double bonds in the α -methylenic systems would be relatively insignificant, the addition serving merely to start the necessary reaction chains. Intramolecular reaction of a type permitting the first-formed diradical $\cdot\text{CH}_2\cdot\dot{\text{C}}\text{H}\cdot\text{CH}(\text{OO}^*)$ to become stabilized by removal of hydrogen from the adjacent α -methylene group [$\rightarrow \cdot\text{CH}:\text{CH}\cdot\text{CH}(\text{OOH})\cdot$] is highly unlikely, since it would not propagate chain reactions.

The Scission Problem.—Organic hydroperoxides, $\text{R}\cdot\text{OOH}$, are, like hydrogen peroxide, effective oxidizing agents for olefinic substances, especially when their decomposition is facilitated thermally or catalytically. The atom of active oxygen in each molecule is applied to the oxidation of susceptible substances within reach. When, however, the radical R is unsaturated, it seems possible that the oxidizing capacity of the $\cdot\text{OO}\cdot$ groups may be applied to the oxygenation of unsaturated centers in the same or nearby molecules in some regulated or standard way which is economical in oxygen. Thus the author has earlier suggested that the secondary reactions of olefinic hydroperoxides may commonly involve one or other of the changes (respectively intra- and inter-molecular):



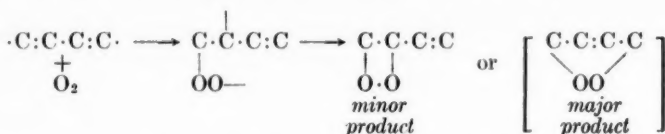
There is no doubt that the $\cdot\text{OOH}$ groups pass in the main, on decomposition, to $\cdot\text{OH}$ groups and that some roughly comparable number of double bonds become simultaneously oxygenated (saturated) and some few become completely severed. Three facts, however, militate against ready acceptance of a general scheme of double bond scissions which starts from the peroxido-olefin and passes, by decomposition of the $\cdot\text{OOH}$ group, through the epoxy compound to ultimate chain-severance. In the first place epoxy groups are saturated in character and when once they are formed normally display a high degree of resistance to further oxidation⁸; at the same time experiments with rubber show that from a dozen to a score or so of molecules of oxygen (ample for a haphazard scheme of attack) may be absorbed for each complete scission effected. Secondly the scission sets in quite unpreventably during the absorption of oxygen by natural rubber (or by shorter-chain polyisoprenes) right at the outset of reaction, and seems to occur with such extraordinary facility that a very direct mechanism may well be suspected. It is this scission which is responsible for the amazing fall in the molecular weight of natural rubber as oxygen attacks it (from 350,000 to 80,000 during absorption of <1 per cent of O_2), and indeed for the characteristic softening and perishing of the rubber. Third, there is the undoubted and compelling fact that a considerable amount of facile and unpreventable scission ordinarily occurs at the β , γ -double bond of sorbic ester and of α , δ -diphenylbutadiene in addition to the more widespread attachment of molecular oxygen at the terminals of the conjugated diene system in each case.

As the 1,4-peroxidation of the conjugated dienes is found to involve the addition of oxygen at the double bond system the reaction presumably starts at one end of one double bond and may conceivably succeed in some degree and in some examples in linking up, at least momentarily, with the other end of the double bond attacked.

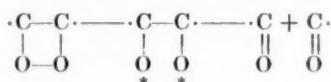
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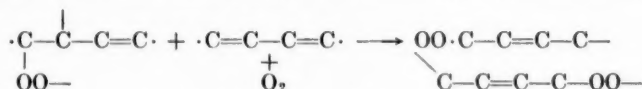
Such a 1,2-peroxide, if it were sufficiently stable to have more than momentary existence, could hardly fail to give the corresponding 1,2-diol on reduction, but in no single one of numerous examples studied has search for a 1,2-diol been successful, although α,δ -diphenylbutadiene gives a small yield of the 1,2-epoxide⁹. Any successful 1,2-linking of oxygen which may occur would thus appear to be of the most transient character and, in so far as it occurs, doubtless undergoes immediate ring-scission, followed by scission of the active diradical to give the corresponding aldehyde or keto fragments:



Such a direct mechanism would be the most economical possible in oxygen, and would explain the apparently utter unpreventability of scission in certain examples where relatively stable 1,4-peroxides form the main product. In the case of monoolefins and unconjugated polyolefins such a scission mechanism might run side by side with normal peroxidation as formulated above, and the degree of its successful occurrence might well be affected by temperature conditions. On the other hand it may quite well be that 1,2-peroxidation has no existence in fact, and that to interpret the experimental observations it is necessary to distinguish clearly between two phenomena, *viz.*: (1) the purely thermal decomposition of peroxidized diene or olefin systems at *a* and *b* in $\cdot\text{O}:\text{O}-\text{CH}:\text{CH}:\text{CH}-\text{CH}\cdot$ or $\cdot\text{CH}(\text{O}:\text{OH}):\text{CH}:\text{CH}\cdot$, and (2) the purely oxidative

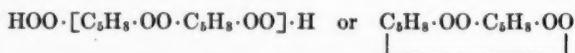
scission of a double bond in a diene or olefin system by the action of external decomposing peroxido groups as though by the action of an added reagent such as permanganate. Since active radicals appear generally to be immediate products of the thermal decomposition of peroxides (decomposition arising at the thermally sensitive $\cdot\text{OOH}$ or $\cdot\text{OO}\cdot$ groups of these) it is perhaps not surprising that the ultimately isolable products of autooxidations carried out at temperatures around or above the decomposition points of the peroxides tend to be a good deal different from those obtained from the same materials at lower temperatures.

The Polymeric Tendency in Peroxide Formation.—As the product obtained by the addition of oxygen at one end of an olefinic double bond could achieve stabilization by intermolecular as well as by intramolecular reaction, it is not surprising that there is a strong polymeric tendency in peroxide formation:



All conjugated di- and triolefinic olefins which have so far been investigated appear to give as the main product mixtures of polymeric peroxides ranging from dimeric to hexameric or octameric complexity; moreover, the yields of the simple dihydroxylated hydrogenation products obtained from these peroxides

in favorable instances appear almost too good to be accounted for by any means of stabilization of the ends of the polymeric chains other than by hydroperoxidation or their direct union. Thus stable dimeric isoprene would be represented by



This polymeric tendency does not disappear in the case of monoölefins and unconjugated di- and polyolefins, and in fact it seems to be general. Even in the characteristic examples of hydroperoxide formation afforded by the cyclohexenes, there is always a polymeric fraction, and the yield of the fraction is likely to depend considerably on the constitution of the olefin and especially on the atoms or groups attached to the ethylenic carbon atoms. The mechanism by which the substituents affect the polymeric tendency may be connected with their efficiency in stabilizing the electrical condition of the radical

center to which they are attached¹⁰, so that the diradical $\begin{matrix} \text{R} \\ \diagup \\ \text{C} - \text{C}(\text{OO}^*) \diagdown \\ \text{R}' \end{matrix}$ will be most stable (and therefore sufficiently long-lived to be able to give polymeric peroxides) where $\begin{matrix} \text{R} \\ \diagup \\ \text{C} - \text{C}(\text{OO}^*) \diagdown \\ \text{R}' \end{matrix}$ are aryl groups, and progressively less stable

for $\begin{matrix} \text{Cl} & \text{H} & \text{Me} \\ \diagup & \diagdown & \diagdown \\ -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_2 \end{matrix}$, and *as-Diphenylethylene*, as shown by Staudinger gives

wholly, or nearly so, high-polymeric peroxides, and among the rubbers the effect of autooxidation on the physical character of the rubber, *e.g.*, as seen in milling, is not a uniform one of mere softening brought about by chain scission. The constitution of the polymers formed from the hydroperoxides of simple olefins or of rubber is likely to be somewhat variable. Experiments with autooxidized rubber have shown that much of the combined oxygen survives in the form of ether links, and in similar experiments with cyclohexenes stable peroxide groups (doubtless of type $\text{R} \cdot \text{OO} \cdot \text{R}'$) have been found together with ether links in the polymeric portion of the autooxidation products. Since, in the case of the simple olefins, polymers which contain both types of oxygen linking can be formed from the peroxides at will, doubtless they arise by direct decomposition of the hydroperoxide-groupings: *i.e.*, $\text{R} \cdot \text{OOH} + \text{R}' \cdot \text{OOH} \longrightarrow \text{R} \cdot \text{O} \cdot \text{R}' + \text{R} \cdot \text{OO} \cdot \text{R}'$. In this way rubber chains may be joined by oxygen links at the same time that they are undergoing scission elsewhere. In addition, some peroxido links between rubber chains, or between different parts of the same chain, possibly are formed independently of this decomposition by union of the $\text{R} \cdot \text{OO}^*$ radicals produced in the early stage of peroxide formation with external

double bonds ($\text{R} \cdot \text{OO}^* + \cdot \text{C}=\text{C} \cdot \xrightarrow{\text{H}^*} \text{R} \cdot \text{OO} \cdot \text{C}=\text{C}^* \longrightarrow \text{R} \cdot \text{OO} \cdot \text{C}-\text{CH}_2 \cdot$). On the whole, the tendency to polymer formation is probably much smaller than with simpler substances, but even a few cross-links in a large molecule have a marked effect on the properties of the rubber.

Analogies from Ozonide Formation.—The evidence of recent years leaves but slight doubt that all organic ozonides capable of isolation contain the peroxido-acetal type of grouping formed by addition of ozone at olefinic double bonds¹². If the addition is considered to follow stages somewhat similar to those discussed above for peroxidation, then thermal scission of the oxygen

Uncatalyzed thermal scission appears to lead largely toward the severing of the O—O link of the peroxide groups, and this is followed by further decomposition of the resulting radicals, which may involve the breaking of some saturated C—C bonds. Polymeric *as*-diphenylethylene peroxide thus gives some benzophenone and formaldehyde by dry-heating, and the formation of formaldehyde by the decomposition of β,γ -dimethylbutadiene peroxide may, as indicated above, quite well be due to the breaking of the α,β -bond in $\cdot\text{O}-\dot{\text{C}}\text{H}-\text{O}-\text{CH}_2-\dot{\text{C}}\text{Me}$: $\text{CMe}\cdot\text{CH}_2\cdot\text{O}-\dot{\text{C}}\text{H}-\text{O}\cdot$. Uncatalyzed decomposition of polymeric peroxides is not very ready at temperatures around room temperature, and apparently it is not very homogeneous as regards the course of reaction. In the case of hydroperoxido-rubber, although scission of the molecules occurs extensively at double bonds in the chains, an appreciable degree of subsidiary scission occurs at C—C bonds immediately adjoining the severed double bonds.

Influence of Combined Sulfur on Chain-breaking.—Although high-sulfur vulcanizates are more prone to undergo deterioration by the action of oxygen than low-sulfur vulcanizates, observation of the action of oxygen on simple saturated and unsaturated sulfides has so far shown no strong tendency for the C—S bond to be broken oxidatively. On the other hand, Armstrong, Little and Doak¹³ have recently shown that ozone causes fairly complete scission of C—S bonds in simple olefinic sulfides.

Softeners and Chain Degradation.—Phenylhydrazine, its salts and numerous accelerators of rather different types when milled into natural rubber cause softening of the mass. In a number of cases examined the molecular weight of the softened material has been found to have fallen substantially (by about 25 per cent) as the result of the milling, and in the case of phenylhydrazine the result appears to be genuinely due to the promotion of increased oxygen uptake¹⁴. Auxiliary substances which are active at all may in general be expected to be effective either in promoting oxygen uptake or in promoting the decomposition of peroxides in a particular way. Success in aiding oxygen uptake is presumably a question of the successful initiation of chain reactions (and likewise successful antioxidant activity of success in chain-stopping) but the effectiveness of both prooxidants and antioxidants is probably much affected by the reaction conditions. Concerning the influence of auxiliary substances on the decomposition of peroxides or peroxide radicals, much remains to be discovered.

REFERENCES

- ¹ Bodendorf, *Ann.* **271**, 1 (1933).
- ² Thoms and Dobke, *Arch. Pharm. Ber. Deut. Pharm. Gas.* **268**, 128 (1930).
- ³ Farmer, Unpublished work.
- ⁴ Sodium sulfite often gives disappointing results as a reducing agent because of its promotion of the side reactions.
- ⁵ Farmer and Sundralingam, in press.
- ⁶ Sundralingam, in press.
- ⁷ Farmer, Koch and Sutton, *J. Chem. Soc.*, **1943**, p. 541.
- ⁸ Yields of epoxide up to 15 per cent survive in the peroxide-catalyzed autooxidation of oleic or elaidic acid at 170°C, but little or none appears to be formed in the photooxidation of methyl oleate at 35°C. The autooxidation of ethylene at higher temperatures yields ethylene oxide in addition to the expected scission product, formaldehyde. This may conceivably arise by decomposition of the diradical $\cdot\text{CH}_2-\text{CH}_2-\text{O}-\dot{\text{C}}\text{H}-\text{O}\cdot$.
- ¹⁰ The *cis* and *trans* configurations at the double bond may have some influence.
- ¹¹ Bolland has recently shown that the thermal decomposition of methyl linoleate hydroperoxide leads immediately to loss of water between $\cdot\text{OOH}$ groups.
- ¹² Rieche, Meister and Southoff, *Ann.* **553**, 187 (1942).
- ¹³ Armstrong, Little and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).
- ¹⁴ Farmer and Naylor, Unpublished work.

THERMAL BREAKDOWN OF RUBBER *

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The degradation of rubber observed during various technological processes may arise from several different causes. Since one such contributory factor is possibly degradation by a purely thermal mechanism, it is of interest to estimate experimentally the importance of this type of degradation under the temperature conditions normally used in the processing of rubber. It may be stated immediately that the authors' experiments confirm that thermal breakdown of rubber is of negligible importance under such circumstances and is always overshadowed by more efficient alternative modes of degradation.

The thermal degradation of rubber, constituting as it does its formally simplest chemical reaction, has real possibilities of giving insight into the chemical stability and reactivity of the rubber molecule. Moreover, the theoretical treatment of the degradation of long-chain molecules has apparently far outstripped the experimental investigation of the problem. To date, attention has been confined to long polymeric chains which are assumed to break in quite random fashion at the regularly recurring bonds joining the monomeric units¹, and it is of importance to see how far this simplifying suggestion regarding the manner of chain scission does in fact correspond to reality. With these two ends in view the writers have investigated the thermal breakdown of rubber in some detail. A preliminary report is now presented on certain complexities of the reaction which may, however, be resolved by consideration of the resonance stabilization of the intermediate degradation products.

In these experiments extreme care was taken to ensure complete removal of oxygen from the rubber before heating at the elevated temperatures necessary for thermal degradation to proceed at a conveniently measurable rate: to this end the rubber sample was cut up very finely and maintained evacuated at 10^{-5} mm. mercury for several days. The rubber used throughout was sol rubber from which the nonhydrocarbon components had been thoroughly eliminated.

At temperatures below 200°C rubber must be considered to be, for all practical purposes, stable: quite negligible reductions in molecular weight were effected by extended periods of heating in this temperature range. At higher temperatures, however, the rubber gradually becomes soft, loses its shape and finally melts to give a slightly yellow, viscous liquid. In the temperature range 220 – 270°C , little or no loss in unsaturation, as indicated by iodine value measurements, accompanies the degradation. In addition, volatile products are formed which careful analysis shows to consist almost entirely of isoprene and dipentene.

When certain quantitative aspects of these observations are examined it becomes clear that thermal fission of the rubber chain does not occur in the random fashion assumed in the various theoretical analyses of the problem.

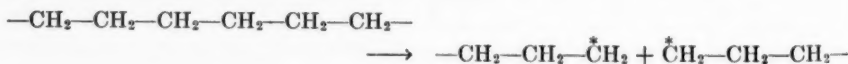
* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 2, pages 133–138, August 1945.

Thus it is found impossible to explain in such terms the observed yields of isoprene or dipentene, either relatively or quantitatively. One example will suffice: after 50 minutes' heating at 250° C the molecular weight of the rubber hydrocarbon, based on osmotic pressure measurements, is reduced to half its original value. In this period about 1 molecule of isoprene and 4 molecules of dipentene are formed for every 100 rubber molecules originally present. If the formation of isoprene and dipentene resulted from the random rupture of the final and penultimate isoprene links in the rubber chain respectively, it may be shown that the yields of the two products would have been equal and would amount to only 0.04 molecules per 100 molecules of rubber.

The apparent activation energies for isoprene and dipentene formation have been determined experimentally at some 52 and 42 kcal., respectively, per g.-mol. The discrepancy between these values and the energy required for the breaking of a normal carbon-carbon single bond (81 kcal.) obviously requires explanation.

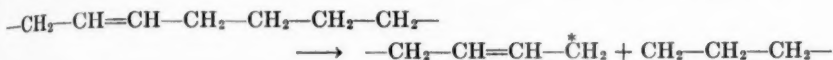
The simple random breakdown theory fails to account for at least one other important aspect of the thermal degradation of rubber: after continued heating at 230–270° C, the molten product first formed gradually becomes more viscous and finally sets to a soft nonsticky solid which is quite insoluble in benzene. This must be interpreted as showing the formation of chemical cross-links between the degraded rubber molecules. A study of the ratio of the osmotic and viscometric molecular weights of soluble degradation products (and, in particular, of fractions into which such products had been separated by the fractional precipitation method) shows that even in the early stages of reaction the molecules acquire a branched structure. Thus a complete picture of the degradation mechanism apparently must involve secondary reactions between the intermediate scission products and other chains.

In such structures as benzene rings or conjugated hydrocarbon chains, the time-average description of the system is not to be taken simply as that corresponding to one single assignment of double and single bonds but as a system in which other bond configurations also play a part, "resonating"—as the phenomenon is termed—with the principal bond structure. For example, not only are the two Kekulé structures involved in the resonance patterns of the benzene molecule but also structures analogous to the three Dewar formulas. In these circumstances quantum mechanical calculations show that the total energy of the resonating system is greater than that which would be calculated when taking into account only the bond energies of the normal structure. Thus one can calculate that this extra stabilizing energy amounts in the case of butadiene (or isoprene), for example, to about 7 kcal. and in the cases of the allyl radical ($\text{CH}_2=\text{CH}-\text{CH}_2$) to 19 kcal. and the ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2$) radical to as much as 30 kcal., these figures being based on the assumed values of 81 kcal. for the normal C—C bond energy and 145 for the C=C bond energy². Obviously, as was first pointed out in this connection by Hückel³, these resonance energies must be taken into account in calculating the total heat changes (ΔH) in reactions involving unsaturated hydrocarbon systems. Thus, while the heat of fission ΔH_f of a fully saturated hydrocarbon chain in the following reaction:



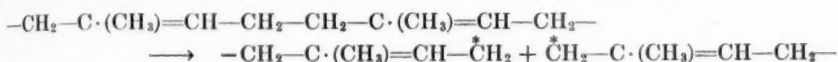
amounts to 81 kcal., in the case of a chain involving one double bond the energy

of splitting the C—C bond in the α -position to the double bond, as follows:



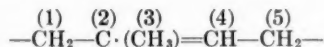
is reduced from 81 kcal. to $(81 - 19) = 62$ kcal. as one of the fission products involved now possesses a resonating allyl radical structure which acquires 19 kcal. resonance energy not present before fission. The heat of fission of any of the other C—C bonds in the above chain is of course normal, *i.e.*, 81 kcal.

In the case of the rubber molecule chain it will again be noted that the heats of fission of the various C—C bonds have all normal values except in the case of the isoprene link. In this case, however, the fission process:



leads to the initial appearance of two allyl radicals at the broken ends of the chain so that ΔH_f is here reduced from 81 to $81 - 2(19) = 43$ kcal. Now, in the above fission reactions leading in each case to the formation of two radicals at the chain ends, there are good reasons for supposing that the activation energies for the fission processes (ΔE_f) are not very much greater than the above quoted values of ΔH_f . At any rate there is no doubt but that the relative order of the three ΔE_f values follows that of the ΔH_f values. Hence it is that the source of the weakness (as suggested by the relatively small ΔE_f value observed) of the isoprene link in rubber, so often commented on in the past, is to be ascribed, not to any real weakness of the electronic binding in this particular bond in the undissociated chain, but to the extra stability conferred by the two allyl radical chain endings obtained after fission has taken place⁴.

Regarding the possible fission of C—H bonds in the rubber chain:

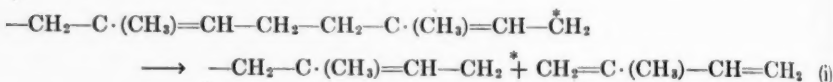


it will be noted that fission of the C—H bonds attached to carbon atoms 1, 3 and 5 leads in each case to the formation of an allyl radical on the chain, so that ΔH_f for these bonds is reduced from the normal value, namely 98 kcal., to 79 kcal. (the normal value probably applies to the case of the C—H link at carbon atom 4). Comparing these values with the value for C—C fission in the rubber chain it will be evident, in thermal degradation experiments at least, that spontaneous C—H fission processes do not compete appreciably at those temperatures at which isoprene link fission first takes place.

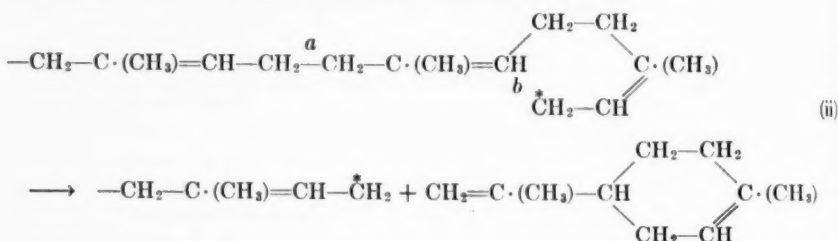
Having dealt at length with the problem of the bond most likely on theoretical grounds to undergo initial fission in the thermal breakdown of the rubber chain, it now remains to consider tentatively the possible subsequent reactions of the free allyl radical endings of these broken chains so as to be able to account for the relatively large amounts of isoprene and dipentene formed, since the experimental data given above indicate that these compounds are not produced by the random splitting off from the ends of stable chains, but probably involve low activation energy processes following directly on a given C—C bond rupture.

Regarding the formation of isoprene, there is little reason to doubt that this is produced mainly by a fission reaction from the end of an already broken

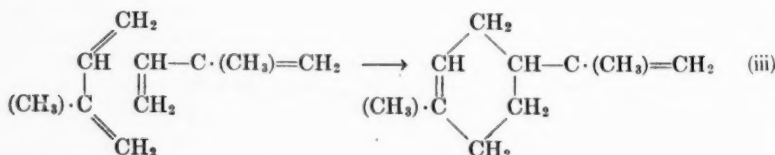
chain of the following type:



the total heat of fission (ΔH_f^i) involved being given as follows: $-\Delta H_f^i = (81 - 19) - (145 - 81 + 7 + 19) = 10$ kcal. The activation energy for this reaction is known much less precisely, but a figure of about 14 kcal. (which is probably of the right order but might be a little low)⁵ has been calculated by Evans and Warhurst⁶. To account for the presence of dipentene in the degradation products, however, the two following possible reactions suggest themselves. First, whenever the radical chain ends of a broken chain acquire the special configuration shown below, a further type of fission, which energetically is more favored than reaction (i), can take place, namely:



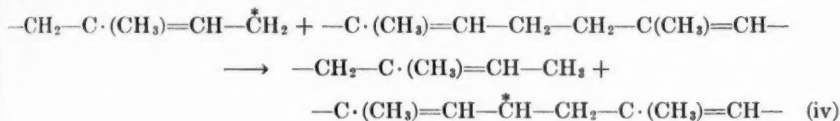
it being supposed that, as the C—C bond marked *a* breaks, a new C—C bond is formed simultaneously across the gap marked *b*. This reaction, which gives dipentene directly in one step, has a zero heat of reaction, for $\Delta H_f^d = (81 - 19) - (81 - 19) = 0$ kcal. Considering the great symmetry exhibited here in the activated state by the reaction complex together with the fact the $\Delta H_f^i - \Delta H_f^d$ is about 10 kcal., it seems reasonably certain to suppose that the activation energy ΔE_f^d for this reaction is considerably lower than ΔE_f^i (the subsequent discussion of the present experimental data shows the $\Delta E_f^i - \Delta E_f^d$ is in fact also about 10 kcal.). The second possible reaction which leads to the formation of dipentene is the well-known Diels-Alder dimerization reaction involving the secondary recombination of isoprene molecules produced by reaction (i) thus:



The heat of formation of dipentene in this reaction would be $2(81) - 2(145 - 81 + 7) = 20$ kcal., while the corresponding activation energy is known experimentally to be about 29 kcal.⁷ Kinetic studies show that the reaction takes place readily in the temperature range 200–300° C, yielding at equilibrium almost 100 per cent dipentene. Hence in all thermal degradation experiments in which the isoprene formed initially is not immediately removed from the temperature of the reacting system, it is certain that this reaction

influences the relative yields of isoprene to dipentene found. In the present experiments all possible care was taken to eliminate the influence of reaction (iii) (1) by freezing out the dipentene and isoprene in a liquid air trap continuously as they were produced during the reaction, and (2) by the use of very thin films of rubber, it having been in fact observed when bulk rubber samples were used that the dipentene/isoprene ratio was increased, presumably because of the intervention of reaction (iii) during the time-lag involved in detaching isoprene molecules formed in the interior of the rubber sample. Thus, whereas in certain experimental conditions both reactions (ii) and (iii) are no doubt involved, it will be assumed in the following discussion, referring to the present experimental results, that the relative rates of production of isoprene and dipentene observed depend on reactions (i) and (ii) above.

The experimentally determined energies of activation for the formation of isoprene and dipentene (say ΔE_i and ΔE_d) are not to be identified directly with ΔE_f^i and ΔE_f^d , respectively; they are in fact composite quantities involving not only ΔE_f^i and ΔE_f^d but in addition the activation energies for the initial formation of the radicals and also the activation energy for the processes which bring reactions (i) and (ii) to a stop. Without making any assumption as to the nature of the last-mentioned type of reaction, it may be stated in general that the energies of activation for radical formation (ΔE_f) and removal appear in ΔE_i and ΔE_d in precisely the same manner in both cases. By way of illustration of this point we may consider what would seem to be the most plausible reaction by which the radical end fragments may be removed:



in which a hydrogen atom is exchanged between an α -methylene group in the body of the rubber chain and a fragment with a radical end-group. The activation energy of this reaction (ΔE_{Ex}) is probably not more than 20 kcal.⁸ and is comparable in efficiency to reactions (i) and (ii). It may then readily be shown that:

$$\begin{aligned} \Delta E_i &= \Delta E_f^i + \Delta E_f - \Delta E_{Ex} \\ \Delta E_d &= \Delta E_f^d + \Delta E_f - \Delta E_{Ex} \end{aligned}$$

Comparison of the difference $\Delta E_i - \Delta E_d$ which has been determined experimentally as $52 - 42 = 10$ kcal. with $\Delta E_f^i - \Delta E_f^d$ which we have shown above to be in the same direction and in all probability to be of the same order of magnitude thus constitutes a partial test of the mechanism of isoprene and dipentene formation suggested above. Further support comes from considering the relative rates of production of dipentene to isoprene which, expressed in terms of the usual reaction rate equations, is simply $(\nu_d/\nu_i) \exp \{(\Delta E_f^i - \Delta E_f^d)/RT\}$, ν_d/ν_i being the ratio of the frequencies with which favorable steric conditions occur for reaction in the two cases. Equating the expression above for the relative rates to that obtaining in the present experiments, namely 4:1, and introducing the known experimental values of the activation energy difference and the temperature, one finds that ratio $\nu_i/\nu_d \sim 2000$, which is in qualitative agreement with our expectation, and that exceptional steric conditions must be satisfied before reaction (ii) can take place.

Finally, it may be noted that if reactions (i), (ii) and (iv) do constitute the essential mechanism of isoprene and dipentene formation, then, since ΔE_{Ez} , ΔE_f^i and ΔE_f^d are all of the same order, the value of ΔE_f which we have estimated to be about 43 kcal. (or just a little greater) should approximate to the the experimental values of αE_i and ΔE_d , as is indeed the case.

It will be evident that our introduction of the resonance concept to provide a convincing explanation of the tendency of the thermal breakdown of rubber to be initiated at the isoprene link leads in point of fact to a satisfactory interpretation of the quantitative experimental data so far available.

ACKNOWLEDGMENT

The authors are greatly indebted to Dr. G. Gee for helpful advice and criticism during the progress of this work, which forms part of the program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

- ¹ See, for example, Montroll and Simha, *J. Chem. Physics* **8**, 721 (1940).
- ² These values are obtained by using the value 168.6 kcal. for the sublimation energy of carbon as recommended by Kynch and Penney (*Proc. Roy. Soc.* **179A**, 214 (1941)). The resonance energies were calculated by using these values and the theoretical methods of treatment of Lennard-Jones (*Proc. Roy. Soc.* **158A**, 280 (1937)) and Coulson (*Proc. Roy. Soc.* **164A**, 383 (1938)).
- ³ Hückel, *Z. Physik* **83**, 674 (1933); *Z. Elektrochem.* **43**, 827 (1937).
- ⁴ In nonthermal excitation processes, e.g., photochemical ones as in the work of Bateman (*Trans. Inst. Rubber Ind.* **21**, 118 (1945)), this may not be the case.
- ⁵ Comparing the ΔH values of this reaction with those of reaction (iv) and noting in this reaction that the resonance energy in the activated state is probably relatively more important than in reaction (iv), it might have been supposed that ΔE_f^i would have been just a little less than one-half the activation energy of reaction (iv) (in the reverse direction), say about 20 kcal.
- ⁶ Evans and Warhurst, *Trans. Faraday Soc.* **34**, 614 (1938); Evans, *Trans. Faraday Soc.* **35**, 824 (1939).
- ⁷ Harkness, Kistiakowsky and Mears, *J. Chem. Physics* **5**, 682 (1937).
- ⁸ Rice and Herzfeld, *J. Chem. Physics* **7**, 671 (1939).

PHOTOCHEMICAL BREAKDOWN OF RUBBER*

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A notable property of rubber and related olefins is their marked photochemical response to weakly absorbed light of wave-length greater than 3000 Å. Although, as in photoinduced halogenation and oxidation, for example, photoactivation of the olefins cannot be generally inferred since the active absorbing entity is or may be the added reagent or a primary reaction product, the photogelling of rubber in a nonabsorbing solvent such as cyclohexane seems free from this ambiguity and points to direct photodecomposition of the rubber molecule. Some authors¹ attribute the cross-linking of the gel state to C-C bonds between ethylenic centers and thereby explain the slightly reduced unsaturation of the gels and their resistance to rubber peptizing agents. Naunton², on the other hand directs attention to the remarkable gelling and reversion powers of minute traces of oxygen, and suggests that the few oxygenated centers which appear to remain even in highly purified rubber³ provide the sites for intermolecular condensation. This latter hypothesis undoubtedly expresses an important mode of cross-linking under certain conditions, but a possible inference that the oxygenated groups are regarded as specifically absorptive and as alone possessing photochemical activity is not in accord with existing evidence. The residual oxygen has been located analytically in hydroxyl groups³ and foreign chromophores are absent in the ultraviolet absorption spectrum of purified rubber⁴. It is therefore difficult to see why the oxygenated fragments should be preferentially activated by irradiation rather than the much more numerous and more absorptive ethylenic units. However, a necessary prelude to further conjecture is fuller knowledge of the basic photochemistry of rigorously isolated rubber. In the work now described, scrupulous care has been taken to free the purified rubber from gaseous contaminants, and chemical changes have been followed directly and not deduced from vague gelation characteristics.

Finely cut intermediate fraction⁵ which was highly pure spectrographically⁶, was contained in a silica tube attached to a vacuum line pumped by Hyvac and mercury diffusion pumps and incorporating in series a trap, a Macleod gauge, and provision for removing gaseous products. After thorough degassing with the trap cooled in liquid oxygen, the pressure was reduced to $<10^{-6}$ mm., and the rubber was then irradiated at room temperature by a mercury arc. Immediate decomposition ensued, as evidenced by the liberation of a gaseous mixture, an observation important not only for its chemical significance but for revealing a means of following the photolysis quantitatively. The rates of gas formation were small (generally $<10^{-7}$ g. mols. per hour under the conditions employed), but could be measured accurately if the Macleod gauge were sufficiently sensitive.

In contrast, chemical examination of the irradiated rubber was severely

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 2, pages 118-122, August 1945.

restricted by the rapid onset of insolubilization. The intermediate fraction gelled so readily that molecular weight and unsaturation changes were unobservable, and data obtained with lower molecular fractions were somewhat equivocal. To cite a typical experiment: 0.35 gram of rubber with initial molecular weight (visc.) 73,500 and iodine value 368 ± 1 liberated 2.15×10^{-7} g. mol. of noncondensable gas (see below) when irradiated for 4.5 hours and then had molecular weight (visc.) 78,500 and iodine value 366 ± 1 . The tendency to reduce unsaturation agrees with results reported for gels prepared in solution.⁷ Further evidence of an increase of molecular complexity on irradiation *in vacuo* was obtained by submitting 60 grams of a high molecular rubber fraction in finely cut form to the full radiation from a mercury arc 6 cm. distant for 170 hours, the containing flask being rotated at intervals. The Mooney plasticities before and after this treatment were 93 and 125, respectively.

The gaseous products of irradiation consist of three fractions: (1) noncondensable at -180° ; (2) condensable at -180° , not at -80° ; (3) condensable at -80° . Fractions (2) and (3) together, usually referred to as condensable gas, account for about 30 per cent of the total when the full emission of the lamp is used, increasing to 40 per cent when irradiation is confined to the 3650 Å. line. The photolyses of olefins in general yield complex mixtures⁸, whose compositions offer but vague clues to the nature of the primary dissociation processes. For the present, therefore, emphasis has been given to determining the probably more informative wave-length dependence of the reaction⁹, but combustion with excess oxygen indicates that the noncondensable fraction is largely hydrogen.

The rate of gas formation is proportional to the light intensity; hence the relative efficiencies of the decomposition at various wave bands can be found by comparing the observed rates at constant intensity (Table I). Two features

TABLE I
PHOTOLYSIS OF RUBBER AT DIFFERENT WAVE LENGTHS

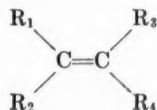
Waveband* (Å)	Rate of total gas formation (g.-mols per sec.)	Relative rate (a)	Relative intensity† (b)	Relative efficiency (a/b)
23-4500	19.89×10^{-12}	1.00	1.00	1.00
23-3400	7.79	0.39	0.24	1.63
2350-2850	3.82	0.19	0.046	4.13
2450-2800	1.55	0.078	0.022	3.55
2850-3400	1.40	0.070	0.13	0.54
2900-3400	1.49	0.075	0.14	0.54
3050-3400	0.73	0.037	0.086	0.43
3050-3950	0.23	0.012	0.086	0.14
3100-4500	0.38	0.019	0.64	0.03
3250-4500	0.14	0.007	0.57	0.01
3500-4500	0.05	0.0025	0.39	0.006
(4100-4500)	0.00 ₅	0.000 ₅	0.052	0.006)

* The principal lines of the mercury spectrum between 2300-4500 Å. are at 2480, 2540, 2650, 2800, 2970, 3020, 3130, 3650, 4050, 4080, 4360 Å.

† 4500 Å. is the approximate limit of sensitivity of the uranyl oxalate actinometer used for estimating the light intensities¹⁰. The solution used transmitted appreciably beyond about 3300 Å. and the observed intensities have been corrected in accordance with the emission characteristics of the lamp.

then stand out: the marked efficiency drop at wave lengths > 2850 Å., and the identification of 3650 Å. as the longest effective wave length in the mercury spectrum, a threshold which evidently reflects the absorption limit. Quanta absorbed at these wave lengths raise the molecular energy by 100 and 78 kcal.

per g.-mol., which are approximately the dissociation energies of normal C-H and C-C bonds, respectively. The normally single bonds of a polyisoprene chain, however, include many whose breaking energies differ greatly from normal, allylic resonance energy reducing that of the α -methylenic C-H bonds to about 80 and that of the central single C-C bonds to about 43 kcal. per g.-mol.¹¹. There is thus a real probability of both C-H and C-C bond scission throughout the active spectral region if the photoabsorbed energy is effectively transferred to the breaking bond. The decomposition is undoubtedly complex, although the efficiency drop at 2850 Å. and the admittedly limited analytical data both suggest that C-H bond scission predominates. This is in marked contrast to thermal degradation, which proceeds exclusively via C-C bond dissociation at a particular link, and is illustrative of the differing energy distributions of photo and thermally activated molecules. Thermally generated vibrational energy is acquired by the molecule as a whole, and the concentrating of sufficient dissociation energy in any one bond is governed by statistical probability principles; the greater the difference between the constituent bond energies, the more will a simple reaction take place, in which the weaker bond is broken. Energy stored in an electronic transition is of less general availability and rarely induces dissociation beyond atoms adjacent to those commonly assigned to the chromophoric group. The present work shows that in the rubber molecule at room temperature either the photoabsorbed energy is not appreciably relayed to the most easily ruptured bond or, if it is, the energy conditions appropriate to subsequent peeling off of volatile, and hence detectable, low molecular units are absent¹¹. Decision between the various modes of C-H and possibly C-C bond scission is difficult, and a detailed definition of the primary dissociation act cannot be given. It is unfortunate in this connection that the electronic basis of low intensity olefinic absorption is so imperfectly understood¹². As Carr and Walker pointed out, the intensity depends on the extent of ethylenic substitution, and it seems likely that the chromophoric character of the group:



as a whole is associated with photochemical activity beyond the double bond.

The difficulty of relating the observed products to the dissociation mechanism in the condensed phase is that the reaction of radicals formed initially with the adjacent substrate may not only reduce the measured quantum efficiency over and above that predicted by the Franck-Rabinowitch principle¹³, but may produce stable molecules irrelevant to the primary breakdown. Only those radicals formed within a few atomic diameters of the surface have a reasonable chance of escaping to combine on the walls of the container; the others undergo reactions such as $H + RH \rightarrow R + H_2$ and $H + >C=C< \rightarrow >CH-C<$. There are several possibilities for secondary reactions; intermolecular cross-linking is clearly important. It follows that gas formation must be regarded as a fractional measure of primary dissociation. A rough estimate of the effect of differing physical states is obtained by comparing the low quantum yield of *ca.* 4×10^{-4} for noncondensable gas formation from rubber in the region 2300–3650 Å. with the corresponding value of 0.3 for isobutene at pressures up to 40 mm. irradiated at 1900 Å.¹⁴, allowance being made for the different spectral ranges.

Rubber displays, in short, those photochemical properties which analogy with simpler olefins would reasonably suggest. Although it cannot be dogmatically stated that the traces of nonhydrocarbon components are completely without effect, there is little doubt that the reaction features described in this paper characterize the polyisoprene molecule as such. The part played by photolysis in certain photoreactions, particularly oxidation, is the subject of separate investigation which will be discussed in due course.

ACKNOWLEDGMENT

The author is greatly indebted to G. Gee and J. L. Bolland for helpful advice and criticism during the progress of this work, which forms part of the program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

- ¹ Pummerer and Kehlen, *Ber.* **66**, 1107 (1933); Meyer and Ferri, *Helv. Chim. Acta* **19**, 694 (1936); Staudinger, *Proc. Rubber Tech. Conf. London*, **1938**, p. 253.
- ² Naunton, *Trans. Faraday Soc.* **38**, 332 (1942).
- ³ Midgley, Henne, Shepard and Renoll, *J. Am. Chem. Soc.* **57**, 2138 (1935).
- ⁴ Bateman and Koch, *J. Chem. Soc.*, **1944**, p. 600.
- ⁵ Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).
- ⁶ Bateman and Koch, *J. Chem. Soc.*, **1944**, p. 600, and unpublished work.
- ⁷ Pummerer and Kehlen, *Ber.* **66**, 1107 (1933).
- ⁸ Noyes and Leighton, "The Photochemistry of Gases", N. Y., **1941**, pp. 21, 419.
- ⁹ Similar work by Asano (*India-Rubber J.* **70**, 307, 347, 389 (1925)) hardly warrants discussion. As smoked sheet containing by analysis 96.5 per cent of hydrocarbon was used and the methods of excluding oxygen appear to be far from stringent, the reaction possibilities are legion.
- ¹⁰ Leighton and Forbes, *J. Am. Chem. Soc.* **52**, 3139 (1930); Forbes and Heidt, *J. Am. Chem. Soc.* **56**, 2363 (1934).
- ¹¹ Bolland and Orr, *Trans. Inst. Rubber Ind.* **21**, 133 (1945).
- ¹² Carr and Walker, *J. Chem. Physics* **4**, 751 (1936); Bateman and Koch, *J. Chem. Soc.*, **1944**, p. 600.
- ¹³ *Trans. Faraday Soc.* **30**, 120 (1934).
- ¹⁴ Kieffer and Howe, *J. Am. Chem. Soc.* **64**, 1 (1942).

RUBBER, POLYISOPRENES AND ALLIED COMPOUNDS.

VIII. THE FORMATION OF DIALKYL SULFIDE DIHALIDES, AND ITS BEARING ON THE PROBLEM OF DETERMINING THE UNSATURATION OF VULCANIZED RUBBER *

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In the course of a fundamental investigation of rubber-sulfur vulcanization it has been found essential to examine critically the unsaturation values obtained by halogenation methods for vulcanized rubber. It has long been known that dialkyl and diaryl sulfides readily add two atoms of halogen to the sulfur atom, and it was realized at once that this type of reactivity would introduce a considerable error into the determination of the unsaturation of olefinic sulfides by halogen addition unless the sulfur-halogen adduct liberates iodine quantitatively from potassium iodide.

Experiments with some simple dialkyl sulfides (Table I) showed that a very considerable uptake of iodine monochloride occurred in an acetic acid medium, and this uptake could be made to proceed to the extent of one molecule of halogen per molecule of sulfide if some mercuric acetate was present. The halogen uptake was not suppressed to any marked degree by the previous addition to the sulfide of methyl iodide or dimethyl sulfate, both of which are known

TABLE I

ABSORPTION OF IODINE CHLORIDE BY SULFIDES IN A MEDIUM CONTAINING ACETIC ACID

Sulfide	Reaction time at 18°C	Apparent iodine value	Mola. halogen consumed per mol. sulfide
Dimethyl sulfide	1 hour	174	0.44
	1 hour	404†	0.99
Di-n-propyl sulfide	1 hour	172	0.80
	2 hours	204	0.95
	1 hour	170*	0.79
	1 hour	180†	0.83
	1 hour	222‡	1.03
	1 hour	226§	1.05
Di-n-propyl disulfide	1 hour	371	2.20
	2 hours	439	2.61
	1 hour	458‡	2.72
	1 hour	330†	1.96
Dibenzyl disulfide	1 hour	300	2.92
	1 hour	395‡	3.85

* Dimethyl sulfate (1 cc.) present.

† Methyl iodide (3 cc.) present.

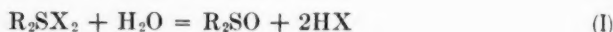
‡ Mercuric acetate (0.5 g.) present.

§ Methyl iodide (3 cc.) and mercuric acetate (0.5 g.) present.

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 64, No. 10, pages 274-278, October 1945.

to add readily to sulfides¹. An even greater halogen absorption was observed with alkyl and aralkyl disulfides, indicating the occurrence of extensive substitutive side reactions.

When the same sulfides were brought into reaction with an excess of iodine monochloride or bromine in carbon tetrachloride and were subsequently treated with aqueous potassium iodide, followed by estimation of the liberated iodine, there appeared to be only a small effective absorption of halogen, although there was every indication of the formation of a halogen adduct, *viz.*, decolorization of halogen and, in the case of dimethyl sulfide, precipitation of a solid adduct. It was obvious, therefore, that when formed in carbon tetrachloride the adduct could liberate iodine fairly completely from aqueous potassium iodide. The difference in the behavior of the adduct in the two types of solvent (acetic acid, carbon tetrachloride) was not due to the polarity of the solvent (Table II), and was attributed to the proportion of the adduct reacting with water in accordance with Equation I instead of with potassium iodide in accordance with Equation II.



When that portion of the adduct which had reacted in accordance with Equation I was taken into account by applying the McIlhiney procedure² the whole of the halogen originally used could be accounted for, so giving no overall halogen absorption except where substitutive side reactions had occurred or where olefinic unsaturation was present.

The proportion of the adduct reacting in accordance with Equation I appeared to be determined by the miscibility of water with the solvent, and the relatively high proportion of acid formed in the presence of chloroform was due no doubt to the improved water miscibility resulting from the small alcohol content of this solvent, since a similar effect was observed when alcohol was intentionally added to a carbon tetrachloride suspension of dimethyl sulfide dibromide. The results for the unsaturated sulfides included in Table II show clearly that, provided the portion of the halogen converted into halogen acid is taken into account, the unsaturation values are satisfactory.

Dialkyl Sulfide Dihalides as Halogenating Agents.—Dialkyl sulfide dihalides have been reacted with olefins to ascertain whether the adduct can transfer its halogen to a double bond and whether any substitutive halogenation is promoted by the active halogen of the adduct (cf. spontaneous conversion of diphenyl sulfide dibromide to 4-bromodiphenyl sulfide). The bromine adducts proved to be very effective bromating agents; cyclohexene, dihydromyrcene and rubber were additively brominated at room temperature with almost complete absence of substitution, the dialkyl sulfide being regenerated. It was found desirable to have the olefin present in excess. Dimethyl sulfide diiodide yielded up its iodine additively to cyclohexene at room temperature, but the rate of iodination was slower than with elementary iodine. Dimethyl sulfide dichloride is not known, but dimethyl sulfide with chlorine itself undergoes substitution and decomposition.

No bromo-ethoxycyclohexane could be detected when cyclohexene was treated with dimethyl sulfide dibromide in a solvent containing alcohol, the inference being that there was no intermediate formation of ethyl hypobromite. This lends support to the opinion expressed above that the formation of halogen

acid on treating dialkyl sulfide dihalides in solvents containing alcohol with aqueous potassium iodide is to be attributed to hydrolysis (Equation I) facilitated by the improved miscibility of water resulting from the presence of alcohol.

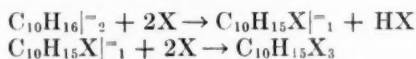
TABLE II
REACTION OF DIALKENYL SULFIDE DIHALIDES WITH AQUEOUS
POTASSIUM IODIDE

Sulfide used	Halogen used	Solvent	Halogen equivalent to I ₂ liberated (%)	Halogen equivalent to HX formed (%)	Total halogen accounted for (%)
Dimethyl sulfide	Br ₂	CCl ₄	96.7	3.1	99.8
Dimethyl sulfide	Br ₂	C ₂ HCl ₃	93.0	7.1	100.1
Dimethyl sulfide	Br ₂	CHCl ₃	38.0	60.5	98.5
Dimethyl sulfide	Br ₂	PhCl	93.3	6.2	99.5
Dimethyl sulfide	Br ₂	C ₂ H ₅ Cl	98.0	1.2	99.2
Dimethyl sulfide	Br ₂	C ₂ H ₄ Cl ₂	72.5	10.5	83.0*
Dimethyl sulfide	Br ₂	PhNO ₂	85.0	15.0	100.0
Dimethyl sulfide	Br ₂	CCl ₄ + 1% EtOH	71.8	28.1	99.9
Dimethyl sulfide	ICl	CCl ₄	86.7	12.9	99.6
Di- <i>n</i> -propyl sulfide	Br ₂	CCl ₄	93.0	5.0	98.0
Di- <i>n</i> -propyl sulfide	ICl	CCl ₄	75.0	24.5	99.5
Di- <i>n</i> -propyl disulfide	Br ₂	CCl ₄	99.0	0	99.0
Di- <i>n</i> -propyl disulfide	ICl	CCl ₄	96.0	3.0	99.0
Diallyl sulfide	ICl	CCl ₄	56.5	4.05	60.55†
Dicrotyl sulfide	ICl	CCl ₄	66.5	7.7	74.2†
Allyl <i>n</i> -propyl sulfide	ICl	CCl ₄	58.6	13.2	71.8†
Allyl <i>n</i> -propyl sulfide	Br ₂	CCl ₄	70.1	0.7	70.8†

* Considerable interaction with the solvent occurred.

† These figures correspond to iodine values 446, 342, 228 and 222, respectively.

Polyisoprenes.—When the foregoing methods were applied to polyisoprene hydrocarbons, the well known readiness with which substitutive and cyclization side reactions occur at once presented difficulties. For, whereas halogen acid formed by substitution must be taken into account to obtain a true value for the additively reacting halogen, any halogen acid produced by halogenation-cyclization³ does not need to be so taken into account, since the reactions:



taking place simultaneously or successively in the presence of an excess of halogen lead to a net absorption of four halogen atoms by the two double bonds involved, which is equivalent to the normal uptake of one molecule of halogen per double bond.

Limitations of the Wijs Reagent.—When the Wijs solution of iodine chloride in acetic acid is used as the additive reagent, the amount of any halogen acid formed cannot be estimated by the McIlhiney procedure, but from the experience of Kemp and Mueller⁴, since amply confirmed in these laboratories and elsewhere, it appears certain that with unvulcanized rubber substitutive side reaction is suppressed by the large amount of acetic acid present, and the total halogen uptake gives a true measure of the unsaturation present. If, however, linkages containing sulfur as sulfide or polysulfide are present, the unsaturation values obtained by the Wijs reagent are likely to be too high in view of the

results recorded in Table I, and this is confirmed by the intentional addition of sulfides or disulfides to rubber (Table III). Moreover the McIlhiney procedure cannot be applied to take into account the halogen reacting in accordance with Equation I, in view of the large proportion of acetic acid present.

TABLE III
APPARENT IODINE VALUES OF RUBBER* IN PRESENCE OF SULFIDES

Sulfide added†	Wij's I.V.
None	358
Dimethyl sulfide	448
Di- <i>n</i> -propyl sulfide	464
Di- <i>n</i> -propyl disulfide	386

* Acetone-extracted crepe is implied by the term *rubber* throughout this paper.

† Added in amount equivalent to 10% sulfur on rubber.

Iodine Chloride in Carbon Tetrachloride as Additive Reagent.—The estimation of the unsaturation of rubber by means of iodine chloride in carbon tetrachloride has also been examined by Kemp and Mueller, whose results indicate clearly that halogen acid is produced in side reactions other than substitution and so must not all be taken into account in calculating the true additive halogenation value. This was demonstrated even more clearly when the iodine chloride-carbon tetrachloride reagent was used for unsaturation determination of dihydromyrcene and squalene (Table IV).

TABLE IV
IODINE VALUES DETERMINED BY IODINE CHLORIDE IN CARBON TETRACHLORIDE

Hydrocarbon	Total I.V.	Iodine equivalent to halogen acid formed*	Apparent additive I.V.
Dihydromyrcene	430	95.5	239
Squalene	406	70	266
Rubber	390	26	338

* Expressed as weight of iodine per 100 grams of hydrocarbon.

Kemp and Mueller have suggested that the halogen acid produced other than by substitution might have arisen from hydrolyzable halogen in the adduct, but experiments in which the iodine chloride adducts of dihydromyrcene and of rubber were isolated and were subsequently treated with water over periods up to two hours revealed no appearance of halogen acid. Kemp and Mueller's suggestion must, therefore, be rejected, and it appears certain that halogenation-cyclization is the correct explanation of the halogen acid formed other than by substitution.

An attempt has been made to evaluate separately the proportions of halogen acid produced by substitution and by cyclization; experiments over considerable periods of time showed steadily decreasing rates of substitution and enabled approximate estimates to be obtained for the amount of substitution occurring during the time normally required for the determination of unsaturation (Figure 1). Using the values so obtained, reasonable unsaturation values have been calculated for the parent hydrocarbons and for samples of rubber to which considerable proportions of di-*n*-propyl sulfide had been added (Table V), although in other instances, *e.g.*, with di-*n*-propyl disulfide, the

amount of substitutively-formed halogen acid appeared to be diminished, and a corrected iodine value could not be calculated.

Bromine as Additive Reagent.—It has been shown in these laboratories⁵ that under suitable conditions a solution of bromine can be used as a quantitative additive reagent for rubber. This reagent has the particular merit of giving no substitutive side reaction, so making more certain the magnitude of

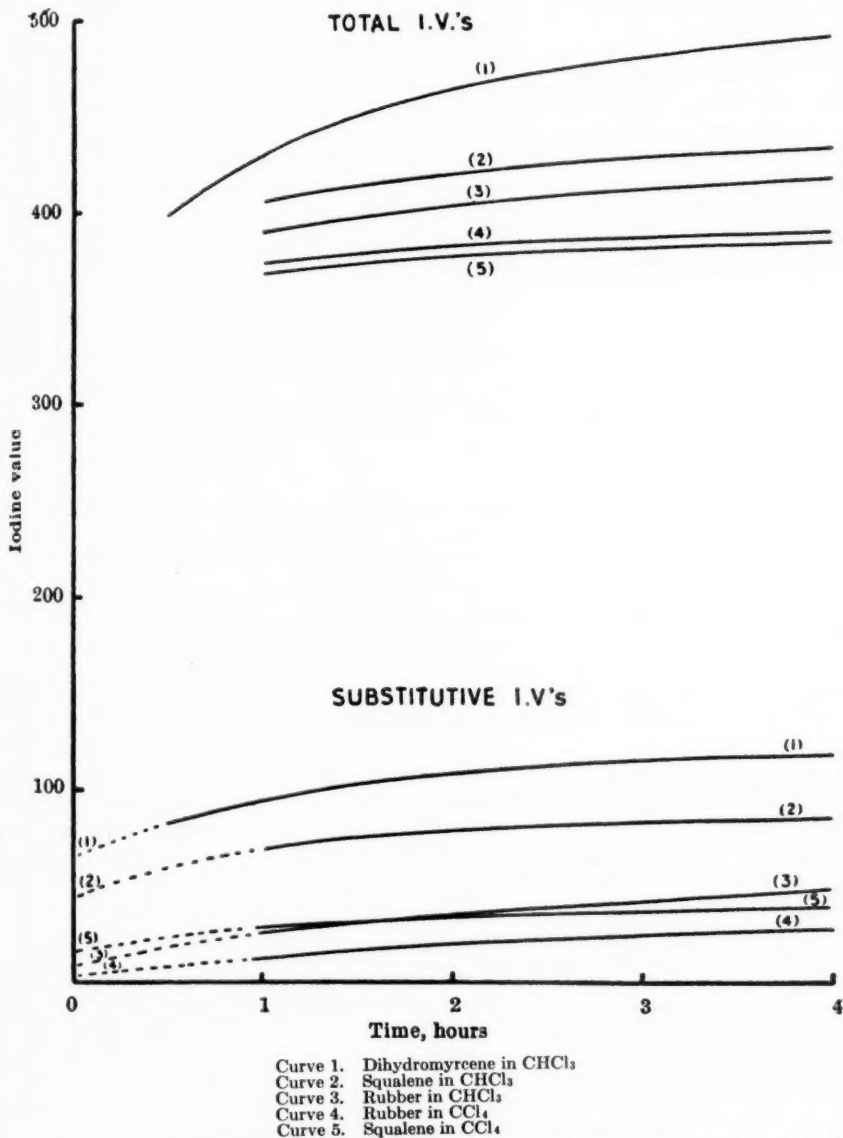


Fig. 1.—Iodine values determined with iodine chloride in absence of acetic acid: dependence of total and substitutive iodine values on time of reaction.

TABLE V
IODINE VALUES DETERMINED BY ICl/CCl₄ REAGENT, CORRECTED FOR
SUBSTITUTIVE REACTION OF HALOGEN

Hydrocarbon	Sulfide added	Total I.V.	Corrected I.V.
Dihydromyrcene	none	430	374
Squalene	none	406	374
Rubber	none	390	358
Rubber	Pr ₂ S	505	356
Rubber	Pr ₂ S ₂	382	not calculable
Rubber	Me ₂ S	551	not calculable

the McIlhiney correction to be applied in the presence of sulfur linkages. A small reproducible proportion of halogen acid is formed by the cyclization reaction, and from knowledge of the amount normally formed from the parent hydrocarbon, any increase due to sulfur linkages can be ascertained and so can be taken into account in obtaining a true value for the unsaturation. The bromine reagent also proves very much more satisfactory than iodine chloride (in carbon tetrachloride) with dihydromyrcene or squalene (Table VI).

TABLE VI
IODINE VALUE OF POLYISOPRENES, DETERMINED BY BROMINE ADDITION

Hydrocarbon	I.V.
Dihydromyrcene	366
Squalene	358
Rubber	357

Application to Vulcanized Rubber.—Increased halogen acid formation due to sulfur linkages has not been observed in vulcanizates containing less than 5 per cent of combined sulfur, and it is considered that the values for total bromine addition provide a satisfactory measure of the true unsaturation. As the sulfur content increases the halogen acid formed does in fact decrease at first, possibly due to the combined sulfur reducing the number of unsaturated centers available for halogenation-cyclization. When the sulfur content is much in excess of 5 per cent, halogen acid formation increases somewhat and uncorrected total bromine addition values must then be regarded as maximum values for the unsaturation.

Wijs iodine values are consistently higher than iodine values calculated from bromine addition (Table VII), doubtless due to preferential reaction of the sulfur-halogen adduct in accordance with Equation I in the presence of the acetic acid in the Wijs reagent.

TABLE VII
UNSATURATION VALUES OF VULCANIZED RUBBER OBTAINED BY ADDITION
OF BROMINE OR OF IODINE CHLORIDE (WIJS)

Sulfur content (%)	Wijs iodine value	Iodine value calculated from bromine addition
None	358	356
1.55	356	341
4.25	326	307
5.9	336	283
8.95	280	254

Figure 2 shows unsaturation values determined by bromine addition in relation to sulfur content; the straight line represents a loss of unsaturation of one double bond for each sulfur atom combined, and the simple rubber-sulfur mixing conforms closely to this relationship. In the presence of zinc oxide, and more especially in the presence of mercaptobenzothiazole and zinc oxide, the loss of unsaturation is substantially less. The interpretation of these results in the light of a comprehensive theory of vulcanization will be presented in a subsequent paper from these laboratories.

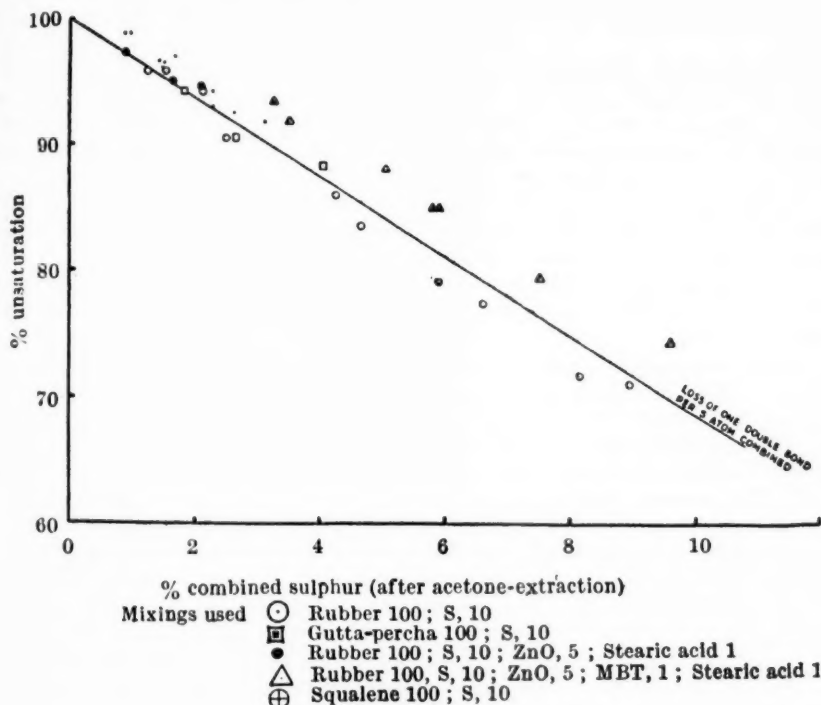


FIG. 2.—Unsaturation of vulcanized rubbers.

EXPERIMENTAL

(Microanalyses were carried out by W. T. Chambers and (Miss) H. Rhodes)

Iodine values of sulfides by the Wijs reagent (Table I).—To the solution of the sulfide (0.1 g.) in chloroform (50 cc.) was added 0.2*N* iodine monochloride in acetic acid (25 cc.). After at least an hour there were added, with shaking, 15% potassium iodide (25 cc.) and water (50 cc.), and the iodine liberated was estimated volumetrically.

Iodine Values of Sulfides by Iodine Monochloride in Carbon Tetrachloride (Table II).—The same procedure was followed, substituting 0.2*N* iodine monochloride in carbon tetrachloride for the Wijs reagent and operating at 0° C. Mercuric acetate could not be used with this reagent. When the McIlhiney procedure was used the liberated iodine was first titrated with neutral thiosulfate, then potassium iodate was added and the additional iodine liberated was

titrated. For unsaturated sulfides rather less substance (0.05 g.) was taken to have present an appropriate excess of reagent.

Determination of Unsaturation of Vulcanized Rubber by Bromine Addition.—In view of the results recorded in Table II, carbon tetrachloride is preferable to chloroform for additive bromination of sulfur-containing substances, but, unfortunately, substitution of the polyisoprene system is appreciable with solutions of bromine in the former solvent. A compromise has accordingly been effected, whereby bromine in carbon tetrachloride has been used as the additive reagent, while a minimum amount of chloroform was used as solvent for the rubber or as a diluent for *p*-dichlorobenzene dispersions of vulcanized rubber.

The finely divided sample (0.08–0.1 g., depending on sulfur content) was dispersed in *p*-dichlorobenzene at 165° C, and to the cooled dispersion was added chloroform (70 cc.). After cooling to 0°, 25 cc. of a 0.2*N* solution of bromine in carbon tetrachloride was added and, after standing for 15–20 minutes at 0° C, the usual procedure was followed.

Reaction of Dimethyl Sulfide Dibromide with Water.—Quantitative reaction occurred on shaking a carbon tetrachloride suspension of the dibromide with water, all of the halogen being accounted for as halogen acid.

Solubility of Dimethyl Sulfide Dibromide in Carbon Tetrachloride.—Iodimetric estimation indicated a concentration of 0.044 g. per 100 cc. of a saturated solution at 0° C.

Brominations with Dimethyl Sulfide Dibromide.—(1) *Cyclohexene.*—Bromine (9.3 g., 1 mol.) in carbon tetrachloride (30 cc.) was added to dimethyl sulfide (5 cc., 1.15 mols.) at 0°. To the cold suspension of dimethyl sulfide dibromide was added cyclohexene (15 cc., 2.5 mols.) in carbon tetrachloride (100 cc.); the dimethyl sulfide dibromide slowly dissolved and gave a colorless solution within 30 minutes at room temperature. Test portions of this solution liberated no iodine from potassium iodide and only a trace of iodine from potassium iodide-iodate. Removal of the solvent yielded 12 g. of 1,2-dibromocyclohexane (b.p. 50°/0.01 mm.), which left no residue on distillation (found: C, 30.05; H, 4.2; Br, 65.7; n_D^{17} 1.548. Calc. for $C_6H_{10}Br_2$: C, 29.75; H, 4.15; Br, 66.1%; $n_D^{22.5}$ 1.544). Repetition in the presence of alcohol (40 cc.) again gave dibromocyclohexane (found: C, 30.4; H, 4.3; Br, 65.2%; n_D^{16} 1.547) as the sole product.

(2) *Dihydromyrcene.*—This hydrocarbon (1.0 mol.) treated with dimethyl sulfide dibromide (2.0 mols.) as above yielded crude dihydromyrcene tetrabromide (70% yield) and no hydrogen bromide. The reaction was slow at room temperature. From the crude oily product the crystalline tetrabromide, m.p. 89° (mixed m.p. with authentic specimen 89°) was easily isolated.

(3) *Rubber.*—An amount of acetone-extracted crepe rubber equivalent to 3 C_6H_8 units, in carbon tetrachloride (2.5% solution), was added to dimethyl sulfide dibromide (1 mol.) prepared as above. All of the reagent was consumed on shaking the mixture for an hour at 15° C, and less than 0.5% of the bromine was found as hydrogen bromide. The product, precipitated by alcohol and vacuum dried, was a tough leathery material. Found: Br, 42.2%; I. V. (Wijs) 128. Calc. for $(C_6H_8)_3Br_2$: Br, 44.0%; I. V., 139.

Iodination with Dimethyl Sulfide Diiodide.—Iodine (0.59 g.) in carbon tetrachloride (50 cc.) was added to dimethyl sulfide (0.2 cc.) in the same solvent (10 cc.), and to the brown solution was added cyclohexene (0.6 cc.). 68% of the iodine was consumed in 22 hours at room temperature (cf. utilization of 88% of iodine in a comparable experiment in which the dimethyl sulfide was omitted).

Brominations with di-n-propyl Sulfide Dibromide.—(1) Cyclohexene.—Bromine (1 mol.) in carbon tetrachloride was added at 0° C to di-n-propyl sulfide (1.25 mols.) in the same solvent. Reaction appeared to be somewhat incomplete, and free bromine was removed by evaporation to small bulk under reduced pressure; the yield of the adduct was 65% of the theoretical. To the cold solution of the adduct was added cyclohexene (3 mols.); the color of the reagent was discharged in 10 minutes. Test of an aliquot portion with potassium iodide and potassium iodate revealed no unconsumed reagent and less than 5% of substitutively-formed hydrogen bromide.

(2) *Rubber.*—To another preparation of the adduct, containing 0.206 g. bromine, was added acetone-extracted crepe rubber (0.4 g.) in carbon tetrachloride solution. The reagent was again completely used up in 15 minutes and only a trace of hydrogen bromide was formed. The product, isolated by precipitation with alcohol, contained 34.4% Br.

Bromination with di-n-propyl Disulfide Dibromide.—A similar procedure was followed, but the yield of the adduct was much smaller (16%). Cyclohexene and rubber were brominated in 10 minutes without hydrogen bromide formation; the bromorubber obtained from 0.2 g. of rubber and an adduct containing 0.05 g. bromine contained 19.75% Br.

SUMMARY

In determining the unsaturation of olefinic sulfides and disulfides by halogenation methods, the addition of halogen to the sulfur atom must be taken into account. The dihalides of dialkyl or dialkenyl sulfides react with aqueous potassium iodide partly to liberate iodine with regeneration of the sulfide, and partly to form halogen acid and dialkyl or dialkenyl sulfoxides. Correction for the latter reaction, which occurs extensively in the presence of alcohol or acetic acid, must be applied before reliable unsaturation values for dialkenyl sulfides can be obtained. With vulcanized rubber and iodine monochloride, the precise magnitude of the correction to be applied is uncertain, but this uncertainty can be removed by using bromine as the additive reagent. Simple rubber-sulfur vulcanizates show a loss of unsaturation corresponding to one double bond per sulfur atom combined up to at least 8 per cent of combined sulfur; vulcanizates accelerated with mercaptobenzothiazole in the presence of zinc oxide exhibit a substantially smaller loss of unsaturation.

The dibromides of dialkyl sulfides readily yield a molecule of bromine to olefins, the reaction being practically exclusively additive.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Ray and Farmer, *J. Org. Chem.* **8**, 391 (1943).
- ² Mellihiney, *J. Am. Chem. Soc.* **21**, 1084 (1899).
- ³ Bloomfield, Part IV, *J. Chem. Soc.*, **1943**, p. 289.
- ⁴ Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
- ⁵ Bloomfield, Part VI, *J. Chem. Soc.*, **1944**, p. 114.

THE PROÖXYGENIC EFFECT AND THE RESULTING DETERIORATION OF RUBBER *

P. CHOVIN

INTRODUCTION

Most unsaturated hydrocarbons unite spontaneously with atmospheric oxygen. Rubber is no exception to this rule, and it may be classed as one of those substances which react slowly with free oxygen. Vulcanization, in spite of improving rubber mechanically, does not make rubber any more resistant to autooxidation; in fact it has just the opposite effect, for the higher the percentage of combined sulfur and the longer the time of vulcanization, the more readily does the rubber autooxidize¹. Vulcanization, then, sensitizes rubber in some way to attack by oxygen.

This harmful action is overcome to a large extent by the use of antioxygenic substances, and it is well known what an important place these valuable catalysts have assumed in present-day technology and to what an extent it is possible to retard the secondary effects of autooxidation, particularly stickiness and softening. On the other hand it is also recognized that rubbers of various origins, when processed under identical conditions perform very differently in service. In these cases analysis shows the presence of elements which may be present only in traces, such as copper, iron and manganese, which promote attack by oxygen, and therefore are to be regarded as the opposite of antioxygenic substances, in other words as proöxygenic substances.

This proöxygenic effect of certain metals is now well understood. Dufraisse and Vieillefosse² have shown that when rubber is masticated on iron rolls, a sufficient quantity of this metal is taken up to contaminate the rubber seriously. A corresponding sample of the same rubber, masticated on wooden rolls, shows much better properties. Taylor and Jones³ found that copper stearate and manganese oleate had a destructive effect when 1 per cent was present in the rubber mixture. As for cobalt salts, it is known that they have already found an industrial application, *viz.*, as a means of degrading rubber to form Rubbone. Finally synthetic rubber, *e.g.*, sodium-butadiene rubber, although very resistant to the action of oxygen, even at 100° C, is rapidly attacked, even at ordinary temperatures, if it contains 2 per cent of copper oleate, manganese oleate or cobalt oleate. Under these conditions up to 10-15 per cent of oxygen may unite with the rubber⁴.

Unquestionably, then, when they act separately and independently, these catalysts accelerate the autooxidation of rubber. This brings up the question as to what happens when they are used in the form of mixtures. It seems clear that what takes place is an action which is called very improperly an induction effect and which might be designated better as a mutual reinforcement of the catalytic action, if the word reinforcement had not already acquired another special meaning in rubber technology. A mixture of catalysts properly chosen

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 1, pages 13-20, January 1942.

and used in certain proportions appears to be more active than the individual component catalysts used separately. Thus Esch⁵, in analyses of crude rubbers of mediocre quality, found three elements present together in every case, viz., iron, manganese and copper, with iron frequently in the highest percentage, in some cases in fact as high as 0.22 per cent. Esch concluded that iron, although not in itself the most active of the elements, is as a result of the promoting action of the elements which accompany it, to be regarded as public enemy No. 1 of rubber.

This mutual exaltation of catalysts has been the subject of extensive investigations in other fields. As an example of autooxidation reactions, manganese oxide and copper oxide are, at ordinary temperatures, separately without action on a mixture of carbon monoxide and oxygen; yet when they are present together (hopcalite) they bring about the union of these two gases. In the field of oxidation by oxidizing agents, the experiments of Krause⁶ on "inorganic enzymes" may be cited. These consist of ternary mixtures of iron oxide, copper oxide and magnesium oxide, which are capable of inducing, much better than any of the oxides individually, or any binary mixture of the oxides, the oxidation of formic acid by hydrogen peroxide. As a final example, chosen in this case from the field of hydrogenation catalysts, may be mentioned the results obtained by Ipatieff⁷ on the activity of copper-nickel mixtures and of mixtures of copper and chromic oxide⁸, both of which combinations are much more effective than the pure metals.

In view of these facts, it seemed of interest to study the mutual reënforcing action of various metal catalysts on the autooxidation of rubber. In the following pages the results of such an investigation are described, the beginning of which has already been the subject of another publication⁹.

EXPERIMENTAL TECHNIQUE

PREPARATION OF THE SAMPLES

Rubbers tested.

Two types of rubber mixtures were used in the experiments: (1) a type akin to so-called "feuille anglaise", or cut sheet, vulcanized by the dipping process, and (2) a mixture containing no antioxygenic substance, and hot-vulcanized. This second type had the following composition:

Smoked sheet	100
Sulfur	2.5
Tetramethylthiuram disulfide	0.2
Benzothiazyl disulfide	0.25
Stearic acid	1
Zinc oxide	5
Clay	40

and was vulcanized with a rise to 143° C in 3-5 minutes, and then 6 minutes at 143° C.

Catalysts.

The catalysts which were chosen were purposely those which are soluble in organic solvents, particularly in chloroform. Various salts of copper, iron, cobalt and manganese were tested, including the following:

Copper salts	Iron salts	Cobaltous salts	Manganous salts
acetylacetonate	acetylacetonate	oleate	oleate
oleate	oleate	linoleate	linoleate
linoleate	linoleate	thioricinate	thioricinate
elaiddinate	thioricinate		nonanoate
stearate	nonanoate	<i>Cobaltic salt</i>	<i>Manganic salt</i>
thioricinate	dibenzoylmethane	acetylacetonate	acetylacetonate
heptanoate			
nonanoate			
undecanoate			
crucate			
diethylthionthiol-			
carbamate			

In addition to these salts, various complex metal compounds were tested, including salts of dithizone, cupferron, mercaptobenzothiazole, α -nitroso- β -naphthol, benzyldioxime, etc.

Chloroform solutions of all these compounds were prepared by dissolving in each case one gram of metal (not of salt itself) in one cc. of chloroform.

Impregnation

The catalysts were added to the rubber samples by impregnation of the latter with the chloroform solutions.

In the case of cut sheet rubber, samples 2 cm. by 0.5 cm. were immersed in the solutions in tared flasks. The difference in weight of a flask before and after impregnation was a measure of the quantity of solution which had penetrated the rubber and, hence, of the weight of metal compound in the rubber sample.

In the case of the hot-vulcanized rubber, the metal compounds were added in a different way. Each sample, cut into cubes 2-3 mm. on a side, was placed in contact with a predetermined quantity of solution. As a result of preliminary tests, the proportion finally chosen was 1 cc. of solution, i.e., 1 mg. of metal, per gram of rubber mixture. This gave a content of proöxygenic metal of 0.1 per cent, based on the rubber mixture. In contact with the solution the rubber swelled, and solvent and proöxygenic compd. penetrated the mass. It was then necessary only to expel the solvent to leave the proöxygenic compd. dispersed alone within the cubes of rubber. This operation was carried out in two different ways, by prolonged heating in an oven (about 2 hours at 70° C), and in other cases by heating in a vacuum (15 minutes at 100° C). The second procedure is preferable because the rubber samples do not begin to deteriorate by autoöxidation during the preliminary operation. During heating in the 70° air oven, on the contrary, incipient oxidation may become appreciable, and since the object is to follow the progress of deterioration of the rubber containing proöxygenic substances by the rate of autoöxidation, this preliminary treatment adds a troublesome complication to the final measurement.

Examination of the individual cubes of the rubber samples after impregnation with the solutions showed that the metal compound did not penetrate uniformly to the middle of the samples. This is a phenomenon which recalls chromatography; a solution in passing through a column of adsorbent gives up gradually to the latter the substances which it contains. In this case a concentration gradient was established, which decreased from the outside to the middle of the cubes. In other words, there was preferential enrichment at the surface.

It was feared that this might have an adverse effect on the reproducibility of the measurements of the rate of autooxidation, but experiments showed that this was not so. Consequently there is no need in such cases to be concerned with inevitable local differences in dispersion in comparing measurements.

EVALUATION OF THE ACTIVITY OF DIFFERENT PROÖXYGENIC SUBSTANCES

Cut sheet.

The use of samples of cut sheet (*feuille anglaise*), grade of rubber which is easily autooxidizable, is of value only as a means of ready classification of catalysts by a purely qualitative evaluation of their effects. Actually, even with proöxygenic substances of moderate activity, samples were totally destroyed in one to two days' exposure to air and light. They were transformed into sticky masses, a perfect example of accelerated deterioration. Only for this reason are these experiments even mentioned.

Hot-vulcanized rubber.

Rubber which has been hot-vulcanized with sulfur is much more resistant than cut sheet (*feuille anglaise*) to autooxidation, and stickiness becomes appreciable, or at the most very slight, at ordinary temperatures only after very long times. Accordingly it seemed advisable in the present work to measure the consumption of oxygen at a temperature considerably above room temperature.

The temperature used in the majority of cases was 80° C, but some tests were carried out at 100° and at 120° C. The apparatus which was used was the manometer of Dufraisse¹⁰. Ten samples of rubber containing the proöxygenic substance and a control sample (treated like the others but with chloroform alone) were placed in the sample tubes connected with the manometric tubes. These sample tubes were brought to the desired temperature, and the air was flushed out by a current of pure oxygen. At the starting temperature of the experiment, closing of the sample tubes makes the mercury rise automatically in each tube to the zero reading of the scale. As a result of consumption of oxygen, the pressure decreases in each sample tube, so that the rise of the mercury in the manometric tube serves as a comparative measure of the autooxidation reactions brought about by the oxygen.

By means of a simple formula, based on the constants of the apparatus, it is possible, if desired, to calculate the volume v of oxygen consumed from the level h of the mercury, *i.e.*, the lowering in the sample tube. This formula is:

$$v = h \left(s + \frac{V - sh}{76} \right)$$

where v is the volume of oxygen consumed at the temperature of the experiment and at atmospheric pressure, h is the level of the mercury in the manometric tube of cross-sectional area s , and V is the initial volume of gas. By this means it is possible to construct curves of the volume of oxygen consumed as a function of time, and thus to deduce the absolute rates of autooxidation. However, the curve $v = f(h)$ is a rather flat parabola, which, for not very high values of h might be mistaken for a straight line. Consequently the volume of oxygen absorbed is roughly proportional to the rise of the column of mercury, at least when this rise does not exceed 20 cm. Since the object is not to obtain absolute rates but only to compare different rates of autooxidation, it is justifiable to use

rate of autooxidation *vs.* rise of mercury-time curves instead of rate of autooxidation *vs.* volume-time curves.

COEFFICIENT OF ACCELERATION

Figure 1 represents, by way of example, the rates of autooxidation, determined at 120° C, of a control sample and of various samples containing 15/100,000, 30/100,000 and 45/100,000, respectively, of copper in the form of copper thioricinate. It will be seen that at this temperature the curves are virtually straight lines. There is, therefore, no ambiguity in defining the coefficient of acceleration due to the proöxygenic substance; it is the ratio of the slope of the curve of the sample containing the proöxygenic substance to the slope of the curve of the control sample.

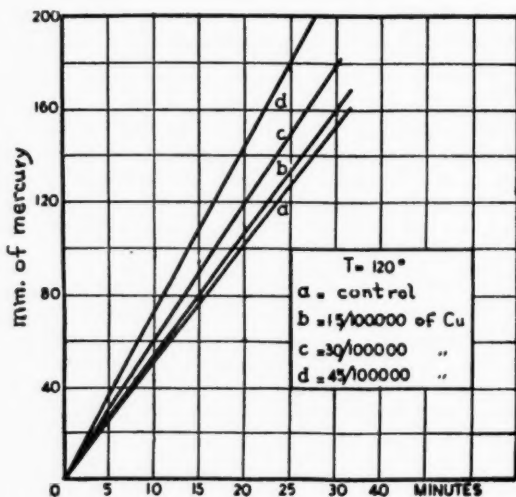


Fig. 1.—Influence of the concentration of the proöxygenic agent at 120° C.

With a copper content of 15/100,000, the acceleration is already appreciable, although slight. The coefficient is 1.03. With a copper content of 45/100,000, the coefficient is 1.50.

It should be noted that the higher the temperature, the smaller is the coefficient of acceleration. Consequently to obtain the most clearly defined results, *i.e.*, with acceleration coefficients considerably above 10, it is advisable to operate at a temperature much lower than 120° C. On the other hand, if the temperature is too low, the rates of autooxidation are too slow, particularly the rate of the control sample, to obtain sufficiently precise measurements. It is advisable, therefore, to operate, as has been mentioned, at 80° C. To make the differences still more pronounced, it is advisable to use a high percentage of proöxygenic substance. This will explain why a content of 100/100,000, *i.e.*, 0.1 per cent, was chosen. At the temperature of 80° C, the curves have different shapes (see Figure 2), and this introduces a new factor which must be taken into account in defining the coefficient of acceleration. The control sample, containing no proöxygenic substance (curve *a*), underwent autooxidation after passing through a rather extended induction period, followed by a uniform

rise in the mercury column. It is this latter part of the curve which represents the desired rate of ascent of the mercury column. On the contrary the curves of the samples containing proöxygenic substances show three characteristic shapes. Curve *b*, with an induction period, is characteristic of curves of relatively weak proöxygenic substances. Curve *c*, which shows no induction period, is representative of rather powerful proöxygenic substances. It is probable that, in this case too, there is an induction period, but that it is extremely short, and that it takes place during the flushing of the apparatus, and therefore escapes measurement. Curve *d*, the concavity of which is downward, is a relatively infrequent type, characteristic of very powerful proöxygenic substances when the attack by oxygen is sufficiently rapid to form on the surface, during the time of flushing the system, a film of deteriorated rubber which obstructs subsequent diffusion of oxygen into the rubber. As a result the rate of oxidation decreases progressively, a tendency which is evident

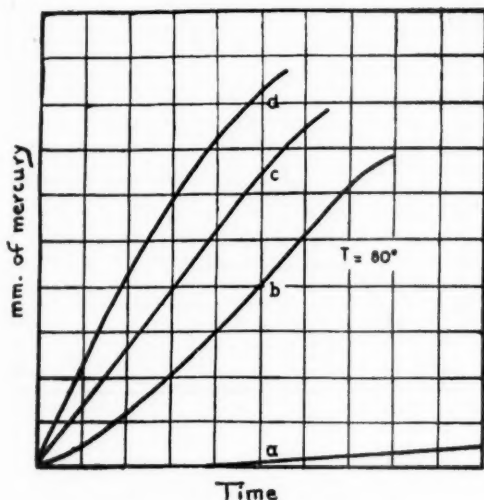


FIG. 2.

at the extremity of curve *c* in Figure 2, and which is absent at times in curves of the type of curve *b*, where the proöxygenic substances are relatively inactive.

The nonrectilinear character of these different curves makes it necessary to choose arbitrarily some basis for defining the coefficient of acceleration with respect to the control sample. In other words, contrary to the behavior of the control sample, at least after it has passed through its induction period, there is here no well defined rectilinear part, or if it is evident, it is only after varying lengths of time, so that any definition of the rate of ascent of mercury loses all meaning if the period when this rate is measured is not specified.

It is with a view to avoiding this uncertainty that the rate of autoöxidation of a sample containing a proöxygenic substance is arbitrarily defined as the rate of ascent of the mercury at the fifth minute of the experiment. From this it follows that the coefficient of acceleration throughout the work which follows is equal to the ratio of the slope of the curve of the sample containing the proöxy-

genic substance at the point corresponding to the fifth minute to the slope of the curve of the control sample in its rectilinear part (see Figure 3).

Nevertheless, it was found that the curves of the relative rates of some catalysts, *e.g.*, cobalt thioricinate and manganese thioricinate, show long induction periods of the order of 1 to 2 hours. However, such cases are relatively rare, and when it was impossible to define the rates to the fifth minute, the slopes of the rectilinear parts of the curves were chosen. This particular method, which is indicated in two cases in Table 2 does not lead to any complications in subsequent tests of binary and ternary mixtures of catalysts, for particular care was taken in these later experiments to choose catalysts with no appreciable induction periods.

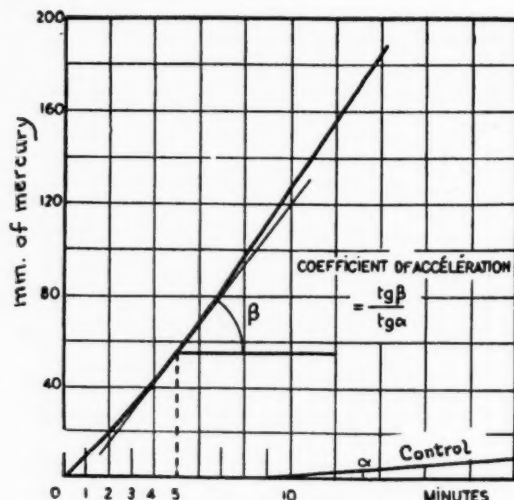


FIG. 3.

EXPERIMENTAL RESULTS

COMPARATIVE ACTIVITIES OF DIFFERENT CATALYSTS

Several different lots of hot-vulcanized rubber, the composition of which has been given, were prepared at the French Rubber Institute. Although each batch was prepared under identical conditions as far as composition, time of mixing, and time and temperature of vulcanization were concerned, the different batches showed differences in their inherent autooxidizability (see Table 1), which were reflected in their induced autooxidizability when catalysts were present. As a result the acceleration coefficient for a given proöxygenic agent depends on the particular batch of mixed stock which is being tested.

TABLE 1

Batch of rubber	Initial autooxidizability (mm. of Hg. per hour)	Ratio of initial autooxidizabilities
1	4.5	1
2	5.4	1.2
3	7.4	1.6
4	11.0	2.4

This is hardly surprising, since in general autooxidation phenomena frequently show irregularities, even when the experiments are carried out with substances which are supposedly pure. It is still more likely, therefore, that rubber, as a highly complex substance, should give very erratic results.

The results of the tests of the different batches indicated two general rules:

(1) With a given proöxygenic agent but with different batches of the same composition, the greater the inherent autooxidizability of a batch, the higher in general is the acceleration coefficient.

(2) The ratio of the acceleration coefficients of two different proöxygenic agents depends on the particular batch of a rubber mixture of any particular composition, and these differences seem to follow no rule in their fluctuations.

From this it follows that if different proöxygenic substances are to be compared, it is essential to confine the work to the same batch. If it is necessary to change to another batch of rubber mixture, the initial autooxidizability of each new batch must be determined.

Experiments at 80° C.

Table 2 gives the acceleration coefficients for various proöxygenic substances, measured at 80° C.

TABLE 2

Metal	Proöxygenic salt (0.1% of metal based on the total weight of rubber mixture)	Batch of rubber	Acceleration coefficient
Copper	Oleate	2	11
		3	14
	Heptanoate	2	12
	Elaidinate	2	10
		1	1.5
	Thioricinate	3	10
	Linoleate	2	8
		1	3.5
	Nonanoate	3	7
	Ethyl acetylacetate	4	3.5
	Undecanoate	2	3.1
		2	2.5
	Acetylacetonate	4	2.5
		1	1.6
	Diethylthionthiolcarbamate	2	1.5
	Piperidinethionthiolcarbamate	1	1.3
Manganese	Linoleate	4	82
	Acetylacetonate (manganic)	4	51
		1	10
	Nonanoate	3	50
	Thioricinate	1	5.5
Iron (ferric)	Acetylacetonate	4	72
	Linoleate	4	30
		1	4.5
	Nonanoate	3	5
Cobalt	Thioricinate	1	12
		3	65
	Acetylacetonate (cobaltic)	4	63
	Ethyl acetylacetate	4	21

An examination of the data in Table 2 will show the truth of the first general rule given above; Batches nos. 1 and 3 showed an initial autooxidizability ratio of 1:1.6. With copper thioricinate, they gave acceleration coefficients of 1.5 and 10, respectively; with copper nonanoate, 3.5 and 7, respectively; with manganese nonanoate, 10 and 50, respectively; with iron nonanoate, 4.5 and 5, respectively; and with cobalt thioricinate, 12 and 65, respectively. It is evident that the greater the initial autooxidizability of a particular batch of rubber mixture, the greater is the coefficient of acceleration with any particular proöxygenic catalyst.

On the other hand, consider two different proöxygenic catalysts, *e.g.*, copper thioricinate and copper nonanoate. With batch no. 1, these gave coefficients of 1.5 and 3.5, respectively. The ratio, $3.5/1.5 = 2.3$, is different from the ratio of the coefficients obtained with the same two catalysts but in another batch of the same rubber mixture, *e.g.*, batch no. 3. Here the ratio is $7/10 = 0.7$. This shows again the validity of the second rule, *viz.*, that it is impossible to foresee the behavior of proöxygenic catalyst in any particular batch of rubber just because its behavior in another batch happens to be known.

Comparative experiments at 80° and 100° C.

Only one experiment will be cited, *viz.*, an experiment on batch no. 3 with copper oleate to show that the acceleration coefficient decreases with rise in temperature. In this particular case the coefficient dropped from 14 to 3.5 when the temperature was raised from 80° to 100° C.

To obtain quick results, one would normally work at some temperature well above room temperature. But it is not advisable to choose too high a temperature, for the lowering of the acceleration coefficients which are generally met with in such a case makes all the experimental results too close together numerically. One might be tempted, then, in order to spread the results better, to operate at a relatively low temperature. But in this case the experiments are tedious and difficult to interpret. For these reasons 80° C was finally adopted as the best temperature.

Experiments at 120° C.

In spite of what has been said above, a few experiments were carried out at 120°, for this temperature is particularly convenient for obtaining rapid results with any given proöxygenic catalyst.

The most interesting result of these experiments is the inversion in the catalytic effect which was found with copper diethylthionthiolcarbamate. This agent is weakly proöxygenic at 80° C (acceleration coefficient only 1.5), but then becomes weakly antioxygenic at 120° C (acceleration coefficient of 0.4). This is a very unusual case, for only in a few instances has copper been reported to have an antioxygenic effect¹².

Influence of some common ingredients in rubber mixtures.

Some experiments were carried out with the object of explaining the action of certain compounding ingredients commonly used in industrial rubber mixtures. Three representative accelerators were tested, *viz.*, mercaptobenzothiazole, benzothiazyl disulfide and tetramethylthiuram disulfide. To the chloroform solution of the proöxygenic agent was added the accelerator in the proportion of one molecule per equivalent of metal. Under these conditions

there was a notable weakening of the proöxygenic activity of the metal compounds studied, the rates of oxidation being reduced to one-quarter to one-half of the original values, according to the combination of metal compound and accelerator.

This is not a case of negative catalysis but of inhibition by suppression of the positive catalyst. In this connection it is of interest to recall that certain commonly used compounding ingredients are capable of neutralizing rubber "poisons".

CATALYSTS IN BINARY MIXTURES

General considerations.

If each metal were to act as if it were alone, without being either inhibited or exalted by another metal, the curve representing the coefficient of acceleration as a function of the composition of the mixture of two catalysts would be a straight line joining the characteristic values of the individual catalysts.

Specifically the coefficient of the rate of a reaction catalyzed by two catalysts can be expressed in the form:

$$k = k_0 + k_1(C_1) + k_2(C_2)$$

where k_0 , k_1 and k_2 are the coefficients of the rate of the uncatalyzed reaction and of the reaction catalyzed by the catalysts C_1 and C_2 , respectively, and where (C_1) and (C_2) represent the concentrations of the catalysts C_1 and C_2 .

In the present case, where the sum of the concentrations of the two catalysts are maintained constant, as will be shown later, the relation can be written:

$$k = k_0 + k_1 + k_1x + k_2(a - x)$$

where x represents C_1 and $a - x$ represents C_2 . Hence:

$$k = k_0 + k_1a + (k_1 - k_2)x$$

The coefficient of acceleration is the ratio of the rate of the catalyzed reaction to that of the uncatalyzed reaction, thus:

$$\frac{1}{k_0} [k_0 + k_1a + (k_1 - k_2)x]$$

which represents a straight line (see Figure 4).

If there were any exaltation of the catalytic action, there would be a fourth term which would depend both on (C_1) and on (C_2) , and the curve would then lie above the theoretical straight line.

It will be shown in the following section that, in the case of binary mixtures of iron, cobalt and manganese salts, all three of the possibilities indicated above are actually encountered.

Choice of catalysts and preparation of samples.

Various catalysts were available, but not all were of equal interest in the work. It was decided to make a judicious choice from these of a few of the most powerful ones, and to study the mutual reinforcing effects or accelerating effects of the resulting catalytic action. The final choice was three catalysts: manganese nonanoate, cobalt thioricinate, and iron nonanoate, which were then grouped in three pairs: manganese + iron; manganese + cobalt, and iron + cobalt.

In all the combinations studied, the sum of the two metals, based on the weight of rubber sample treated, was maintained constant at 0.1 per cent. In each test, eleven sample tubes in the Dufraisse manometer were used. Hence, for each combination of metals, A-B, eleven samples were prepared by placing in eleven small round-bottom flasks solutions of A and of B in quanti-

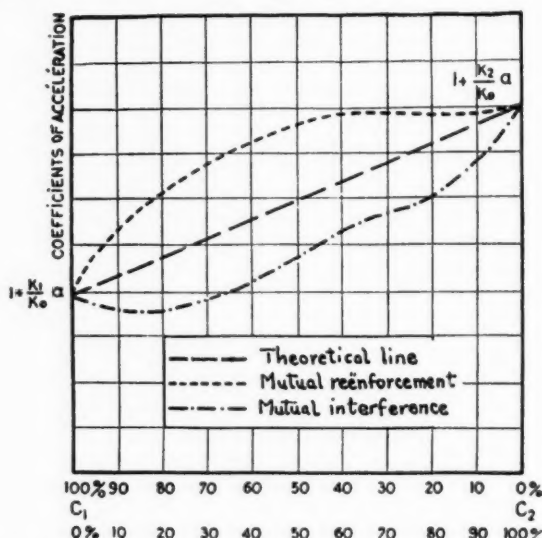


FIG. 4.—The coefficient of acceleration as a function of the composition of the mixture of catalysts.

ties such that the total volume was 1 cc. (see Table 3); to each was then added 1 gram of rubber sample cut into very small pieces. The samples were allowed to swell, and the solvent was then expelled by heating under vacuum. Samples impregnated with the two catalysts, A and B were thus obtained, with the sum of A and B remaining constant, and A and B varying as shown in Table 3.

TABLE 3

	1	2	3	4	5	6	7	8	9	10	11
cc. of Solution A	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0
cc. of Solution B	0	0.10	0.20	0.30	0.40	0.40	0.60	0.70	0.80	0.90	1.00

Examination of various binary mixtures.

(1) *Manganese-iron combinations.*—The experimental curve for these mixtures (see Figure 5) approximates the theoretical straight line for mixtures containing proportions from iron 100%-manganese 0% to iron 70%-manganese 30%. Within this range, each catalyst behaves as if it were present alone. On the contrary, in the range which extends from iron 70%-manganese 30% to iron 0%-manganese 100%, the experimental curve lies above the theoretical straight line throughout. There is, then, a decided exaltation effect, which reaches its maximum intensity with the mixture of the composition: iron 50%-manganese 50%.

With this 50:50 composition, the coefficient of acceleration is 49, whereas it should, according to the law of mixtures, with no exaltation effect, be only

27.5. This means that the exaltation effect has increased the acceleration coefficient by $100 \times (49-27.5)/27.5 = 78$ per cent of its theoretical value.

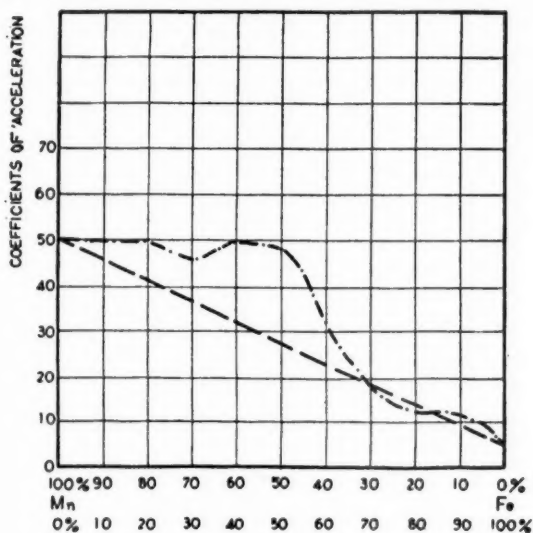


FIG. 5.—Binary mixtures of manganese and iron.

(2) *Manganese-cobalt combinations*.—With these combinations, the experimental curve lies below the theoretical curve throughout. Hence in all proportions, each catalyst has an adverse effect on the activity of the other catalyst (see Figure 6).

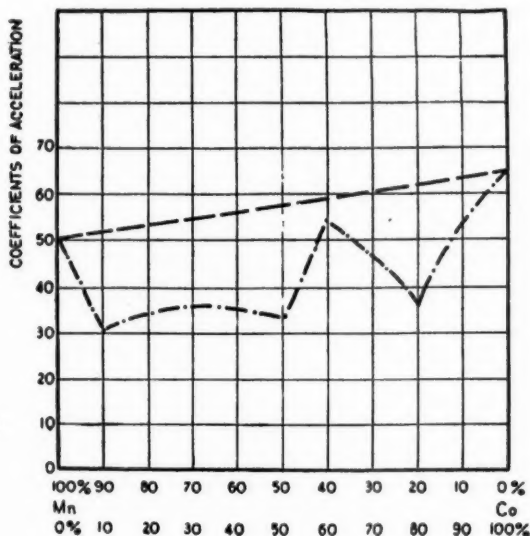


FIG. 6.—Binary mixtures of manganese and cobalt.

(3) *Iron-cobalt combinations.*—With these combinations, the curve is partly above and partly below the theoretical curve (see Figure 7). The point of inversion lies approximately at the mixture containing iron and cobalt in the proportions of 30 and 70 per cent. With higher proportions of iron there is an exaltation effect; with lower proportions a retarding effect. The maximum exaltation effect is found at a point corresponding approximately to the composition of iron 80%—cobalt 20%. The acceleration coefficient γ then reaches about three times its theoretical value, an indication of a very marked effect.

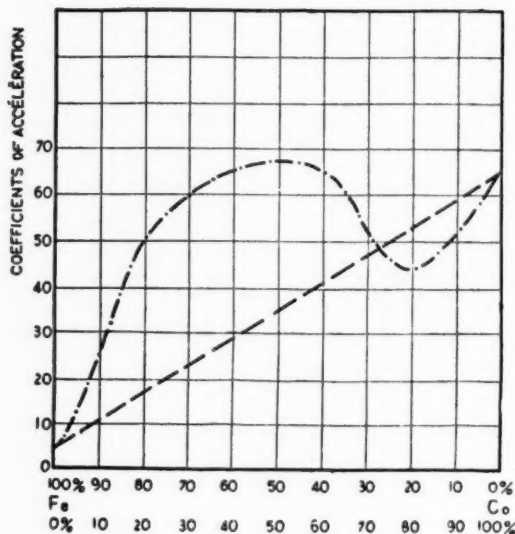


Fig. 7.—Binary mixtures of iron and cobalt.

CATALYSTS IN TERNARY MIXTURES

In view of the results with binary mixtures, it was of interest to test ternary mixtures in the same way. Here too it would have been possible to study all triple combinations of the various catalysts, but the number of experiments involved in such a systematic series would have been too great. The actual experiments were therefore limited to one particular case, that of a mixture of iron nonanoate, manganese nonanoate and cobalt thioricinate, with a total content of 0.1 per cent, based on the rubber sample.

Choice of compositions of the mixtures.

In these experiments, the problem was to cover all possible mixtures of three components, A, B and C, the sum of which was to be constant and equal to 1 cc., by varying the content of each component by 10 per cent changes. The method was to take for A successively 1 cc., 0.9 cc., 0.8 cc., etc., then to take for the sum B + C the complements to unity of these values, i.e., 0, 0.1 cc., 0.2 cc., etc. This gave, as shown in Table 4, all possible combinations for the sum B + C.

TABLE 4

A	B + C	B	C
1	0	0	0
0.9	0.1	0.1	0
		0	0.1
0.8	0.2	0.2	0
		0.1	0.1
		0	0.2
0.7	0.3	0.3	0
		0.2	0.1
		0.1	0.2
		0	0.3

etc.

A convenient way of calculating all these compositions is to resort to the classic method of triangular representation. Assume the equilateral triangle ABC shown in Figure 8. Every point P lying within the triangle represents the

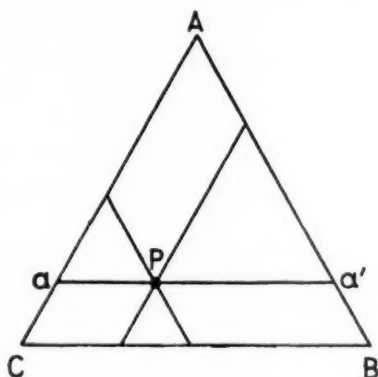


FIG. 8.

composition of a ternary mixture of the components, A, B and C. To determine the composition represented by point P, it is necessary only to draw through this point lines parallel to the three sides of the triangle, and to consider the segments intercepted by these parallel lines on the sides.

The content of component A, for example, is proportional to the length of the equal segments intercepted on the two sides of the triangle starting from angle A and lying between the side opposite A and line parallel to this side (BC) passing through P, in other words, aC' or aB' .

To represent all the points which are concerned in the experiments described, it is necessary only to divide the sides of the triangle into ten equal parts and to draw through these points lines parallel to the three sides, as in Figure 9. There is thus obtained a triangular network system, in which all the points of intersection correspond to the compositions given in Table 4. The three vertices of the triangle correspond to the pure individual substances; the points along the sides of the triangle correspond to binary mixtures; the points within

the triangle correspond to ternary mixtures. This gives, in all, sixty-six different points. It will be seen that line CB has only eleven points; it was possible therefore, to study in a single operation all the corresponding compositions, since the manometer was equipped with just eleven sample tubes. After that, the next step was to study in one operation the compositions corresponding to the line 1-1' and vertex A, lines 2-2' and 9-9', lines 3-3' and 8-8', lines 4-4' and 7-7', and finally 5-5' and 6-6', since all the points on the pairs of lines totaled just eleven for each point.

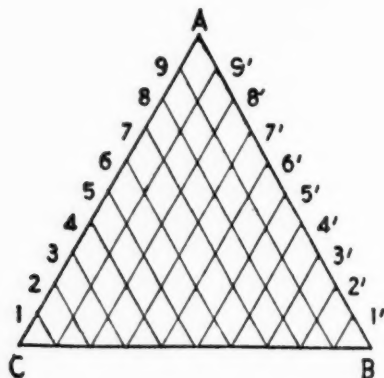


FIG. 9.

Examination of the ternary mixture: iron nonanoate-manganese nonanoate-cobalt thioricinate.

As a convenient way of calculating the results, one may assign to each point an index equal to the coefficient of acceleration of the particular mixture of catalysts, the composition of which corresponds to the point in question. Lines of equal acceleration can then be drawn, so that a diagram like Figure 10 is obtained.

These lines of equal acceleration can be represented in a different way by extending, at each point on the diagram, the acceleration coefficients on lines perpendicular to the base triangle. The positions of these points determine a surface S , and the intersection of this surface S by planes parallel to the base triangle determines the lines of equal acceleration in space. Their projection on the base triangle is none other than Figure 10 itself.

To find out in any particular case whether there is an exaltation effect, it is necessary only to compare the surface S with the plane P which passes through the three points representing the individual catalysts. Actually this plane P is merely the location of the theoretical coefficients of acceleration which would be obtained by application of the law of mixtures to the three catalysts. There is an exaltation effect at every point on the surface S which lies above the corresponding point on plane P .

It is obvious that a large part of the surface S is located above the plane P . In an approximate way, the projection of this portion of the surface on the base triangle is contained within the two sides extending from the vertex B (iron) and a more or less sinuous line joining the vertex C (manganese) to a point a located on the opposite side.

It is especially interesting to determine the compositions of the ternary mixtures whose coefficients of acceleration are greater than the coefficient of the most powerful individual catalyst, cobalt. These points are located within the surface bounded by the line of acceleration coefficient equal to 65. This surface is cross-hatched in Figure 10.

There is also a "culminating point", corresponding to the composition: cobalt-manganese-iron 1:1:3, and for which the coefficient of acceleration is 75. The acceleration coefficient increases, then, from a value of 65 for cobalt alone to 75 for this ternary mixture. At this point the theoretical coefficient of acceleration is only 26, so the exaltation effect has increased the coefficient almost three-fold.

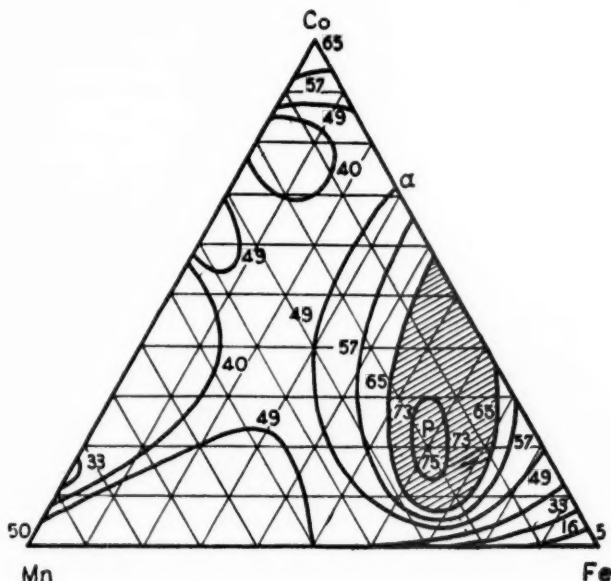


FIG. 10.

According to the terminology introduced by Ipatieff, Corson and Kurbatov³, this ternary mixture of cobalt, manganese and iron salts in the ratio 1:1:3 (of metals), which represents the maximum intensity of action, is the "eucoactive mixture".

CONCLUSIONS

Three particularly important conclusions can be drawn as a result of the investigation described in the present paper.

(1) The proöxygenic effects of the various organic salts of copper, iron, manganese and cobalt which were tested are not confined to the surface alone. All these salts are soluble in organic solvents, and it is to be presumed that they are likewise at least slightly soluble in rubber hydrocarbon. Actually it was observed that immediately after impregnation of rubber with the solution, the proöxygenic substance had penetrated into the interior of the sample,

although this penetration was not uniform. This concentration gradient resulted in a preferential attack at the surface by gaseous oxygen. This attack was manifest in the formation of a sticky surface coating which acted, to a certain extent, as an obstacle to further penetration of oxygen into the core of the small pieces of rubber. It was also observed that, after autooxidation, deterioration of the samples was chiefly on the surface. This deterioration was very pronounced, *e.g.*, even after only 15–30 minutes in the manometer at 80° C; the pieces of rubber adhered strongly to one another.

(2) When present as binary mixtures, salts of manganese, iron and cobalt showed true mutual exaltation effects in their catalytic activities. A mutual inhibitory effect was likewise observed in some cases.

(3) In the form of ternary mixtures, and within a limited range of compositions, these same salts induced more rapid autooxidation than was to be expected of them by application of the law of mixtures. This effect was particularly great with a eucoactive mixture of cobalt, manganese and iron salts in the proportion of 1:1:3 (based on the metals), in which case an exaltation effect 300 per cent of the calculated effect was found.

REFERENCES

- ¹ Dufraisse and Étienne, *Congrès intern. caoutchouc*, Paris, 1937, Recueil des communications, p. 101; *Rev. gén. caoutchouc* **14**, No. 137, 9 (1937); **15**, 12 (1938); *RUBBER CHEM. TECH.* **11**, 282 (1938); Dufraisse and Le Bras, *RUBBER CHEM. TECH.* **12**, 805 (1939); *Rev. gén. caoutchouc* **18**, 79 (1941); Kemp, Ingmanson and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939).
- ² Dufraisse and Vieillefosse, *Rev. gén. caoutchouc* **11**, No. 102, 5 (1934).
- ³ Taylor and Jones, *Ind. Eng. Chem.* **20**, 132 (1928).
- ⁴ Wolshinski and Loginowa, *Kauchuk i Rezina* **1940**, p. 41.
- ⁵ Esch, *Gummi-Ztg.* **52**, 1301 (1938).
- ⁶ Krause, *Ber.* **72**, 161, 637 (1939).
- ⁷ Ipatieff, *Bull. soc. chim. France* [5] **7**, 281 (1940).
- ⁸ Ipatieff, Corson and Kurbatov, *J. Phys. Chem.* **44**, 670 (1940).
- ⁹ Chovin, *Compt. rend.* **212**, 797 (1941).
- ¹⁰ Dufraisse, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, 1937, p. 489; *Proc. Rubber Tech. Conf. London*, 1938, p. 547; *RUBBER CHEM. TECH.* **11**, 268 (1938).
- ¹¹ Dufraisse and Chovin, "Handbuch der Katalyse", G. Schwab, Vienna, 1940, Vol. 2, p. 352.
- ¹² See, for example, Baur and Obrecht, *Z. physik. Chem.* **41B**, 167 (1938).

A NEW MATERIAL: ANHYDRIDE RUBBER. I *

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In earlier work¹ on the action of various unsaturated compounds on rubber, Compagnon and the present author described briefly a new reaction of maleic anhydride. It should be added, as a matter of record, that the reaction of maleic anhydride and rubber had already been studied by Bacon and Farmer², who, in a very interesting work, described a process for obtaining addition products of rubber and maleic anhydride. It is well, therefore, first of all to describe the principle of their work and the results which were obtained.

The first observation made by Bacon and Farmer was that when a toluene solution of milled crude rubber is heated for several hours at about 100° C with maleic anhydride in the presence of benzoyl peroxide, which acts as a catalyst, a definite reaction takes place. The reaction product can be precipitated by alcohol, and can then be recovered in the form of a white or pale yellow resin which does not have any of the elastic properties of rubber. In a more extensive investigation of the reaction, where the experimental conditions were varied, *e.g.*, the proportions of benzoyl peroxide and of maleic anhydride, nature of the solvent, concentration of the solution, and time and temperature of heating, Bacon and Farmer succeeded in obtaining a true series of addition products, whose properties changed progressively with the proportion of chemically combined maleic anhydride. With increase in the proportion of maleic anhydride, there was a gradual transition from products which were still somewhat rubbery to fibrous products, and finally to hard brittle resins which contained more than one-third by weight of chemically combined maleic anhydride and which had none of the physical properties characteristic of rubber. As might be expected, the solubilities likewise changed progressively from products which were soluble in rubber solvents to those which were soluble in solvents for maleic anhydride; *e.g.*, some of the derivatives were soluble in boiling ethyl alcohol.

In the reaction discovered at the French Rubber Institute, a product was obtained which behaved like rubber and had its general characteristics, but in addition possessed certain peculiar properties which warranted it being regarded as a true modified rubber. Perhaps the main idea in the previous work of Bacon and Farmer was to obtain such a product, but, if so, very special operating conditions would have been necessary.

The present author has found that the reaction can be started by milling, a strange and unexpected phenomenon which points to a part played by complicated physical and chemical factors, probably specific to the reaction, since no success has been attained up to the present time in reproducing the reaction by any other means.

A discussion of how to interpret the chemical processes involved in the two different modes of action of maleic anhydride on rubber, *i.e.*, the reaction in

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solution and the reaction on a mill, is withheld until later in this work; at this point the most important features to be considered with respect to the reaction on a mill are:

- (1) the conditions under which the reaction is carried out;
- (2) the properties of the product obtained;
- (3) the extension of the reaction to other monomeric vinyl compounds.

By comparing this last point with the combination of the same vinyl compounds with rubber hydrocarbon in latex form, the only logical conclusion is that the reaction is a copolymerization.

CONDITIONS OF THE REACTION

The action of maleic anhydride on rubber is induced by passage of a mixture of the two between the tight rolls of a mill. The reaction is evident in a particularly striking way with proportions of maleic anhydride of the order of 5 to 10 parts by weight per 100 parts of rubber. After a certain time of milling the mixture gradually loses its plasticity, the sheet becomes more nervy and drier, and its edges become ragged. The reaction is accompanied by an intense crackling noise.

Without going further it should be stressed that the reaction is not started by the heat evolved by the milling operation; on the contrary heating has an unfavorable influence, and for combination of rubber and maleic anhydride to take place, it is necessary to mill the mixture on a cold mill. This observation furnishes a parallel with the only other reaction now known which is induced by milling, *viz.*, plasticization, which progresses, as was made known by the work of Cotton³ and of Busse⁴, through the intermediate action of oxygen. Another striking similarity between plasticization and the reaction of rubber and maleic anhydride is the fact that plasticization also proceeds more rapidly under cold conditions than under hot conditions.

Still another point worthy of note is that the addition of peroxidic catalysts, such as benzoyl peroxide, accelerates combination with maleic anhydride. It seems probable, then, that in the absence of these catalysts, the peroxides which are formed when rubber is milled⁵ take part in the reaction, a likelihood which would appear to be supported by the inhibitory effect of a large number of substances such as hydroquinone, phenyl- β -naphthylamine, trinitrobenzene, and sulfur. With respect to this last phenomenon, attention should be called to the relation which suggests itself between this phenomenon and the phenomenon of minimum oxidizability observed by Dufraisse and Étienne⁶, the influence on the aging of fabrics treated with latex reported by Stevens and Gaunt⁷, and the protective action against the deterioration of crude rubber by light observed by Blake and Bruce⁸. In addition, there is to be considered the inhibitory action of phenols, quinones, amines, etc., on polymerization⁹.

But even if the operating conditions which are effective for plasticization are similar to those effective for the reaction of rubber and maleic anhydride, the transformations which rubber undergoes in the two processes are wholly unlike. For simple mastication makes rubber more plastic and more soluble in solvents, whereas in the presence of maleic anhydride the reaction which takes place results in a less plastic and less soluble rubber.

Should this be interpreted to mean that, under these particular conditions, oxygen no longer plays an active part? This would be a bold conclusion to draw, and all that may be said is that in this sort of contest between the two

reactions which have such opposite effects, the effect of maleic anhydride finally prevails.

The novel character of this phenomenon would seem in itself to be sufficient to warrant a more extensive study with a view to helping explain the mechanism of mastication. But added to this theoretical aspect of the problem was the more immediate prospect that the very unusual properties of the product would offer interesting technical applications.

PROPERTIES OF THE PRODUCT

It has already been mentioned that, by its reaction with maleic anhydride, rubber is rendered drier and acquires more nerve. With a sufficiently high proportion of maleic anhydride, the sheet is observed to change so much that it actually becomes crumbly. However, if at this stage milling is continued, or better still, if a plasticizing agent is added, the ragged pieces mass together again, and a continuous sheet is obtained.

Rubber modified in this way has hitherto unknown properties; it is, for example, much less soluble and much less thermoplastic. It is not necessary, in order for these changes to be appreciable, to carry the reaction to the extreme stage described above. The change in chemical structure is so well defined that combination of only 1 per cent of maleic anhydride on the mill is necessary to obtain a product which, although apparently similar to ordinary masticated rubber, has become to a great extent insoluble in benzene. This fact in itself makes evident the fundamental difference between this compound and the compounds obtained in the reactions described by Bacon and Farmer. In a study of their method by the present author, the products which were obtained were still soluble in benzene even when they contained as high as 10 and 20 per cent maleic anhydride.

In an attempt to define the product obtained on a mill, it might be said that it is akin at the same time to both crude rubber and to vulcanized rubber. Like crude rubber it can be milled, calendered, extruded, etc., and, in general, shaped into any desired form. Like vulcanized rubber, it is almost insoluble in solvents and merely swells to a slight extent. Small pieces of modified rubber, placed in test-tubes, covered with benzene, and allowed to stand for fifteen months swelled slightly but remained otherwise practically unaltered, whereas a control sample of crude rubber which had been milled alone under the same conditions formed a completely fluid solution. Modified rubber shows a certain degree of elasticity, and has little tendency to adhere to itself, and it is much less thermoplastic than ordinary crude rubber. These properties of modified rubber, combined with the fact that it is still amenable to processing, would seem to make it particularly adaptable to new applications.

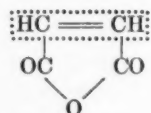
Perhaps the unusual character of the substance and its resemblance to both crude and vulcanized rubber can be appreciated best by from the viewpoint that its behavior is similar to that of crude rubber when it is subjected to high compressive forces, but that it behaves like vulcanized rubber when it is compressed relatively little.

EXTENSION OF THE REACTION TO OTHER MONOMERIC VINYL COMPOUNDS

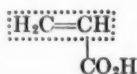
Transformations similar to those with maleic anhydride were observed with other ethylene derivatives, particularly vinyl compounds such as acrylic acid

and acrylonitrile. But in addition to the operating difficulties involved in their use because of the volatility of these products, the effects obtained are less marked, and are characterized chiefly by lessened solubility.

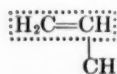
However, in all cases, the changes are sufficiently well defined to warrant the conclusion that it is the active double bond of maleic anhydride which takes part in the reaction, since this active double bond is the only structural feature common to the three compounds.



maleic anhydride



acrylic acid



acrylonitrile

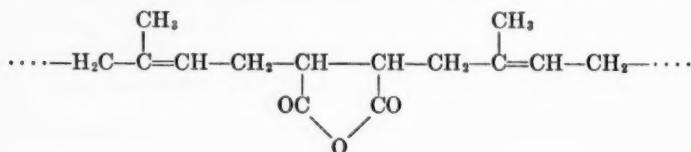
Based on the experiments which have been described, it would appear that the reaction is a general one, and one would seem justified in expecting it to be applicable to vinyl derivatives in which the vinyl residue is attached to at least one atom or group of atoms of electronegative character. Experiments by the present author, which will be described in detail later, were carried out on a whole series of agents having to a greater or less degree the characteristics just mentioned; among others, acrylic esters, styrene, citraconic anhydride, itaconic anhydride, crotonic acid, etc.

REACTIONS BETWEEN RUBBER AND MALEIC ANHYDRIDE

In a later paper, the process of combination of rubber and maleic anhydride will be discussed from the purely chemical point of view. But first of all it is well to state precisely what is meant by copolymerization, a term which was used in the foregoing discussion for the reaction which takes place on a mill. When copolymerization takes place between rubber and a vinyl derivative, there is union between the rubber hydrocarbon chains or fragments of these chains by means of vinyl or polyvinyl groups, in which case the monomer may already be polymerized to a more or less advanced degree before union with the rubber chains or chain fragments takes place. The links of the rubber hydrocarbon chain, *i.e.*, the isoprene groups, and monomeric vinyl groups can in this way form all sorts of configurations from chain structures to very complex networks.

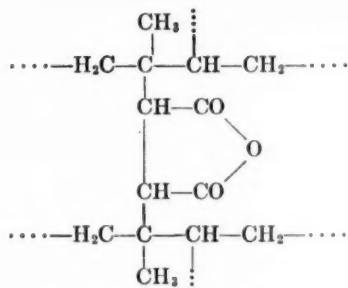
In choosing copolymerization as the proper term, it is assumed that the reaction involves basically the formation of compounds, the simplest members of which conform to the following configurations.

(1) Union into chains of isoprene groups, maleic anhydride entering between two links of the rubber hydrocarbon chain after rupture of the latter:



(2) Formation of bridges between chains by fixation of maleic anhydride on two carbon atoms of two different double bonds, *e.g.*, as in the following

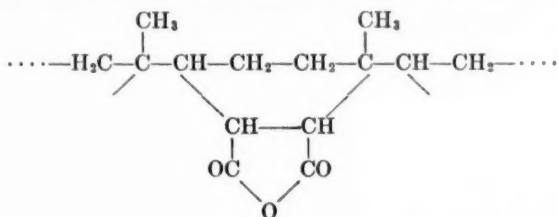
scheme:



Obviously this last structure is the more probable, and the formation of such intermolecular bridges, corresponding to what is at present accepted as taking place in the process of vulcanization¹⁰, would explain well the particular phenomena which were observed.

It should be added that the links thus established between the molecules or fragments of molecules of rubber hydrocarbon are necessarily short, because maleic anhydride is not polymerizable, and therefore they are limited to a single maleic anhydride residue. Nevertheless it was proved some years ago that, in spite of maleic anhydride not being polymerizable, it still is capable of uniting olefin compounds by what has been termed additive heteropolymerization. This particular type of copolymerization applies, for example, to styrene¹¹, vinyl acetate¹² and vinyl chloride¹³.

In discussing the mechanism of the reaction which they studied, Bacon and Farmer took into consideration the possible reactions outlined above. In addition they suggested the possibility that maleic anhydride is fixed between two neighboring double bonds of a single molecule of rubber:



In view of the fundamental differences between the physical properties of the products obtained by the solution method and by the milling method, it is only right to assume that the chemical structures of these two products are likewise different. It is not beyond the realm of possibility that, in dilute solutions, the probabilities of union between different chains are less than when combination takes place within the mass of rubber itself. If so, in the latter case a network structure would predominate. On the other hand the powerful degrading action of the peroxides formed during milling should make possible the formation of a structure in which the isoprene fragments are relatively short. The only way to make this point certain is by ozonolysis reactions.

PRACTICAL APPLICATIONS OF ANHYDRIDE RUBBER

The peculiar properties of the modified rubber which has been described, and which has been designated by the term "anhydride rubber", made it of

interest to study directly its various possible applications. The results obtained up to the present time will be described in a series of papers to follow the present paper, which attempts only to point out the potential value of the reaction. In the next paper, P. Compagnon, to whom credit is due for the greater part of the original work on the reaction of rubber and maleic anhydride, will point out the principles of the maleic anhydride reaction and the possibilities of vulcanizing the products obtained. This work will serve then as a starting point for those interested in the applications of these products. Following this there will be described, among other applications, those which have received particular attention at the French Rubber Institute and which have been the subject of special study by A. Jarrijon.

However, a brief survey of these possible applications may be of interest at this point. They will, above all, depend on the peculiar stiffness of the crude products, which show maleic anhydride to be an unusually effective stiffening agent, capable also of reducing the thermoplasticity of rubber. These properties should be of particular advantage in the manufacture of extruded hose, etc., which will not flatten or sag during vulcanization in an autoclave and likewise in the production of articles more or less complicated in shape. Their sheets, tenths of a millimeter in thickness, can be calendered successfully, and these can be hung on a metal wire in an autoclave and vulcanized in open steam without losing their shape by flowing. Ebonite made from the new modified rubber shows an improvement in one of the principal faults of the ordinary product, its tendency to soften around 60° C. Certain electric properties also are different. A greater resistance to the action of solvents is also shown by anhydride rubber, e.g., a sample of tubing made of the latter swelled in oil but retained its shape when immersed in hot oil under conditions where a corresponding sample of tubing made of ordinary rubber disintegrated. At the same time a sample of ebonite made of modified rubber was superior to a corresponding sample of ebonite made of ordinary rubber.

These few examples will make evident the field which is open for the use of the new type of modified rubber, and it is believed will make an interesting contribution to the rubber industry.

REFERENCES

- ¹ Compagnon and Le Bras, *Compt. rend* 212, 616 (1941); *Rev. gén. caoutchouc* 18, 89 (1941).
- ² Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, 1938, p. 256.
- ³ Cotton, *Trans. Inst. Rubber Ind.* 6, 487 (1931); *Rev. gén. caoutchouc* 8, No. 75, 179 (1931).
- ⁴ Busse, *Ind. Eng. Chem.* 24, 140 (1932).
- ⁵ Dufraisse and Yvielefosse, *Rev. gén. caoutchouc* 12, No. 114, 3 (1935).
- ⁶ Dufraisse and Etienne, *Rev. gén. caoutchouc* 14, No. 137, 9 (1937); 15, 12 (1938); *RUBBER CHEM. TECH.* 11, 282 (1938).
- ⁷ Stevens and Gaunt, *Proc. Rubber Tech. Conf. London*, 1938, p. 686.
- ⁸ Blake and Bruce, *Proc. Rubber Tech. Conf. London*, 1938, p. 736.
- ⁹ Carothers, Williams, Collins and Kirby, *J. Am. Chem. Soc.* 53, 4203 (1931).
- ¹⁰ Le Bras and Compagnon, *Chim. & Ind.* 46, 291 (1941).
- ¹¹ Wagner-Jauregg, *Ber.* 63, 3213 (1930).
- ¹² I. G. Farbenindustrie A.-G., A. Voss and E. Diekhäuser, German patents 540,101 and 544,326 (1930).
- ¹³ I. G. Farbenindustrie A.-G., British patent 466,898 (1937).

ANHYDRIDE RUBBER. II

PRODUCTION AND VULCANIZATION *

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In the first part of this work¹, Le Bras described the interesting characteristics of the product obtained by combination, on a mill, of rubber and maleic anhydride, and he called attention to the useful potentialities of this reaction in connection with the reaction described previously by Bacon and Farmer².

It is intended in the present part of the work to give, first of all, some practical information on the way that the reaction can be carried out. But, since the new modified rubber must be vulcanized to be of any practical value, and since, as might be expected, the conditions of vulcanization are not the same as for ordinary rubber, the means which have been found for carrying out this operation are described. It is obvious that, because of the many accelerators and combinations of accelerators which might have been tried, there was no pretention of obtaining ideal results in this first work; however, since the results which have been obtained so far are sufficiently promising to be of practical value, a description of the method of vulcanization which has already been developed should be useful as a basis for further work by those who may be interested in these reactions.

EFFECT OF MILLING ON A MIXTURE OF RUBBER AND MALEIC ANHYDRIDE

When rubber which has already been plasticized is placed on a cold tight mill and 1 to 2 per cent of maleic anhydride is added, it will be found that instead of becoming more plastic and more tacky, the rubber becomes "drier" and apparently more nervy. A sample of this modified rubber when immersed in benzene or gasoline, instead of dissolving readily, forms only a gel. If milling is continued for a longer time, the behavior of the rubber follows a normal course, and its plasticity increases progressively.

If, instead of adding 1 to 2 per cent of maleic anhydride, 5 to 10 per cent is added to the rubber, the changes which take place during milling become still more sharply defined. Figures 1, 2 and 3 show these three characteristic stages.

In Figure 1, a mixture of rubber and 8 per cent of maleic anhydride has been milled insufficiently for any appreciable reaction to take place; the rubber forms a continuous sheet of ordinary appearance on the rolls. In Figure 2 a reaction has taken place, and the rubber has changed completely in appearance. This transformation is accompanied by a violent crackling noise which is of an entirely different character from that noticed when vulcanized rubber is passed between the rolls of a mill. When this crackling ceases, the reaction is complete, and it is at this moment that the rubber has the driest and most ragged appearance. If the milling is continued, the product becomes plastic again, as

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 3, pages 79-84, March 1942.

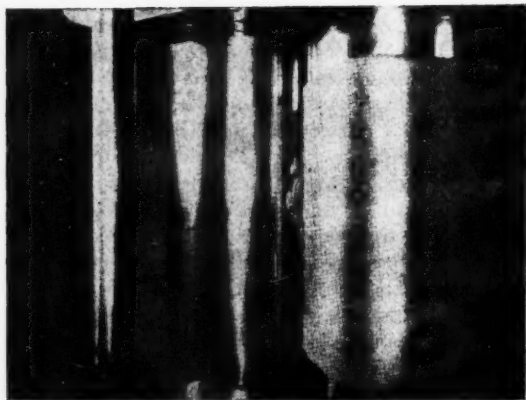


FIG. 1.—Maleic anhydride has been added to the rubber, but the reaction has not yet taken place.



FIG. 2.—The reaction has taken place. The product is dry and ragged.

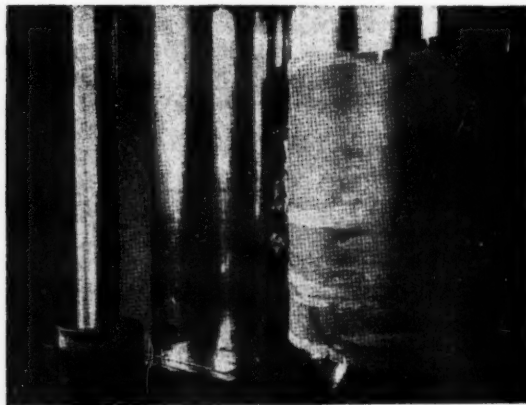


FIG. 3.—The product of the reaction is re-plasticized and forms a sheet.

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is shown by Figure 3, which gives a good idea of the sheet obtained by this additional milling. It will be noticed that, even though the rubber forms a uniform sheet around the front roll, it does not form an ordinary rolling bank as in the case of ordinary milled rubber.

It is of interest to follow, as the milling is continued, the behavior of the products in solvents. It has already been pointed out in earlier papers³ that the products are insoluble in solvents. This can be seen in Figure 4, which shows two samples of rubber which have been immersed for one hour in benzene after having been milled for the same length of time, in one case rubber alone (the left hand sample in the photograph), in the other case rubber with 8 per cent of maleic anhydride (the right-hand sample in the photograph). In this

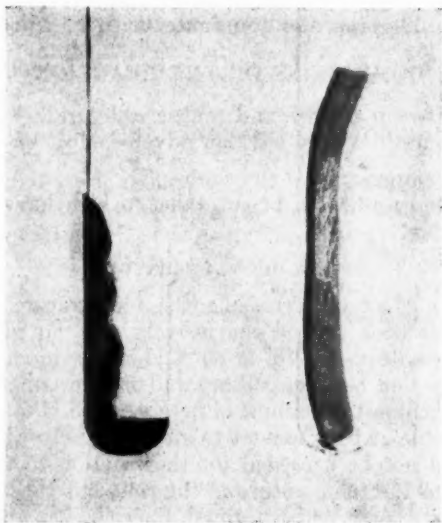


FIG. 4.—Action of benzene on rubber which has been milled with maleic anhydride (on right), and has been milled without maleic anhydride (on left).

experiment the milling was sufficiently long for the reaction between rubber and maleic anhydride to progress to completion and for the mixture to become plastic again.

The action of benzene on rubber mixtures containing 1 to 10 per cent of maleic anhydride, and with the reaction having been carried to different stages, was followed quantitatively. Some of the results are shown in Table 1, and from them certain generalizations are possible.

(1) After addition of maleic anhydride to the rubber on rolls which are just tight enough to assure its incorporation into the rubber, the mixtures dissolve completely in ordinary solvents.

(2) When the mixing is carried out on a tight mill, a definite reaction sets in and at this point the products dissolve only partially and leave a residue which is merely swollen. After a given time of reaction, the higher the percentage of maleic anhydride the less is the swelling, and the smaller is the proportion of rubber which goes into solution. With a given percentage of

maleic anhydride, the more the reaction has progressed, the less the swelling and the smaller the fraction which is dissolved by the benzene.

(3) Further milling after the reaction is completed, with the object of replasticizing the product, does not seem to increase appreciably the swelling and the proportion insoluble in benzene, at least for products containing relatively high proportions of maleic anhydride. On the contrary it is a well known fact that milling has a very marked effect on the behavior of normal crude rubber toward solvents, in that the longer the time of milling the less viscous are solutions of the milled rubber.

The time required for the reaction between rubber and maleic anhydride to take place depends chiefly on the number of passes of the mixture through a tight mill. Consequently the time for the reaction on any particular mill depends on the quantity of the mixture, *e.g.*, it was found that 5 minutes was necessary with 100 grams and 45 minutes with a 1 kilogram.

CONDITIONS OF THE REACTION

The reaction between rubber and maleic anhydride takes place readily. However, certain conditions may have an adverse effect on its progress:

- (1) Too high a temperature of the rubber;
- (2) The preliminary addition of substances which have an inhibitory influence on the reaction.

EFFECT OF TEMPERATURE

The unfavorable effect of increasing the temperature has already been pointed out¹. It has been proved conclusively that no reaction takes place when the mill rolls are heated at 70° or 80° C; likewise it was found impossible to carry out the reaction between rubber and maleic anhydride in a Werner mixer, for in this machine the amount of heat evolved is too great.

It is hardly possible at the moment to state precisely what temperature of the mill rolls should not be exceeded for the reaction to take place, for the essential factor is not the temperature of the rolls but the temperature of the rubber at the instant when it passes through the rolls, *i.e.*, at the moment when the reaction supposedly takes place. This temperature, which is difficult to estimate, depends on the tightness of the rolls, on their speed and friction ratio, and particularly on the quantity of rubber being milled, which governs in effect the rate of cooling and the size of the bank, which is itself heated in the milling process. For practical reasons, it is well to operate with mill rolls cooled to 15–20° C and to use a small enough quantity of rubber so that there is practically no bank between the mill rolls. Under these conditions there is no advantage in cutting the rubber mixture with a knife during milling as is customary in ordinary mixing.

The rolls need not be of unequal speeds for the reaction to take place. However, there is a decided advantage in a differential speed of rolls as far as the quality of the vulcanized product is concerned, but because of the heating effect this is possible only with relatively small quantities of rubber. As an example, on a laboratory mill, with rolls 20 cm. in diameter and 34 cm. working length the reaction takes place very satisfactorily even with a friction ratio corresponding to roll speeds of 10 and 19 meters per minute, respectively, and a temperature of the rolls which does not exceed 40° C, provided that only 100–200 grams of rubber is milled. On the other hand, if 1 to 1.5 kilograms of rubber is used, which is the maximum quantity for the particular mill, it is

best to operate with practically no friction ratio and with a roll speed of 10 to 12 meters per minute.

Tightness of the rolls is an indispensable condition for the reaction; however, when much rubber is to be milled, it may be of advantage to have the rolls slightly more open.

ACTION OF INHIBITORY AGENTS

It has been found that by adding certain substances to rubber before adding maleic anhydride, the reaction between rubber and maleic anhydride proceeds to only partial completion or even can be completely inhibited. By adding 1 per cent of a series of substances, it was found that only oxidizing agents and reducing agents had an inhibiting action, particularly products used in the rubber industry as vulcanizing agents, accelerated and antioxygenic substances.

Among oxidizing agents, trinitrobenzene, benzoquinone and tetrachloroquinone, inhibit the reaction completely, and anthraquinone has a very marked inhibitory action. Benzoyl peroxide on the contrary acts as a positive catalyst of the reaction.

Among reducing agents, the vulcanizing agent sulfur, the accelerator selenium diethyldithiocarbamate, and the antioxygenic compounds phenyl- β -naphthylamine and hydroquinone, inhibit completely the reaction. Tetramethylthiuram disulfide and pyrogallol have a partial inhibitory action. Among reducing agents which have no inhibitory action are glucose and phenol.

In contrast to these, vulcanizing agents such as phosphorus pentasulfide and pentamethylenediamine tetrasulfide, accelerators such as zinc diethyldithiocarbamate, diphenylguanidine and hexamethylenetetramine, and the antioxygenic compound aldol- α -naphthylamine have no inhibitory action.

TABLE I

Maleic anhydride (percentage on rubber)	Time of milling on a tight mill after adding maleic anhydride (minutes)	Visible changes	Swelling in benzene (percentage)	Rubber dissolved (percentage)	Swelling in benzene (percentage) after heating 0.5 hr. at 143° C
1	1	complete reaction	jelly	—	—
	2	plasticized	dissolved	—	—
	5	plasticized	dissolved	—	—
3	1	incipient reaction	1050	—	—
	2	complete reaction	875	—	—
	5	plasticized	jelly	—	—
6	0	—	dissolved	—	jelly
	1	incipient reaction	750	35	625
	2	complete reaction	500	15	400
	20	plasticized	610	15	475
10	0	—	dissolved	—	jelly
	1	incipient reaction	600	25	500
	2	complete reaction	475	10	375
	20	plasticized	300	8	250

Among other substances tested, those which were neither reducing agents or oxidizing agents were found to be without inhibitory power; in fact, active fillers such as carbon black, zinc oxide and magnesium carbonate seemed to have positive catalytic effects.

PLASTICIZATION

No truly systematic work was done on plasticization; however, it can be said that, in an approximate way, rubber-maleic anhydride mixtures can be readily plasticized as long as the proportion of maleic anhydride added to the rubber does not exceed 10 per cent. As an example, a smooth homogeneous sheet was obtained by milling for several minutes on a mill at 40° C and 30 r.p.m. (even speed rolls) 100 grams of the product obtained by the reaction of 8 parts of maleic anhydride and 100 parts of rubber.

PROPERTIES OF PLASTICIZED ANHYDRIDE RUBBER

The properties of the unplasticized products which physically are always more or less ragged, are not such as to make the products of much interest. But when these products have been plasticized, they can be sheeted out, and then become of interest both in relation to crude rubber and to vulcanized rubber. Masticated crude rubber has, of course, properties very different from those of vulcanized rubber. Apart from its solubility in solvents, masticated crude rubber is very plastic and can be easily compressed into any form by relatively slight pressures. Vulcanized rubber, on the contrary, resists relatively high pressures without being appreciably deformed permanently. When placed in contact two sheets of masticated crude rubber stick easily together and form a homogeneous unit, and the same effect is obtained when two sheets of unmasticated crude rubber are placed in contact at a higher temperature. On the contrary, two sheets of vulcanized rubber cannot be made to adhere readily whatever the pressure applied and whatever the temperature of the sheets. Finally the contrast between the load-release curves of crude and vulcanized rubber is a familiar one; the hysteresis cycle of crude rubber and its permanent deformation are much greater than those of vulcanized rubber.

What is particularly curious about anhydride rubber is that it resembles at the same time both crude rubber and vulcanized rubber. Its similarity to vulcanized rubber, already mentioned in connection with the action of solvents, is evident in Figures 5 and 6. Figure 5 shows a sheet of plasticized anhydride rubber and a sheet of ordinary milled rubber side by side. Figure 6 shows the stress-strain curve and hysteresis cycle of a sheet of anhydride rubber and the stress-strain curve of a sheet of masticated rubber. As is evident in Figure 6,

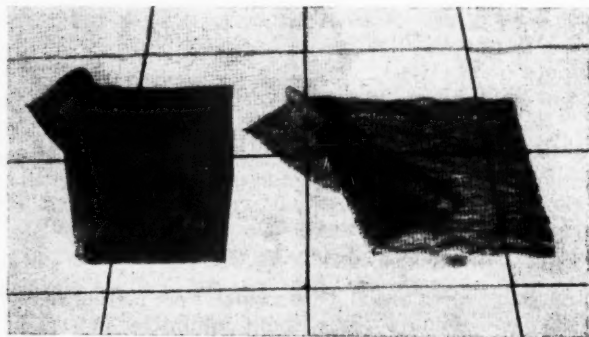


Fig. 5.—At left. Anhydride rubber after the reaction and plasticization. At right. Rubber milled alone under the same conditions.

the tensile strength of the modified rubber, although higher than that of ordinary rubber, is nevertheless very low.

Anhydride rubber resembles vulcanized rubber also in its behavior when hot and when very cold. Unlike ordinary rubber, it does not flow at 150°C , and at -20°C it is still flexible at the end of two hours, when under the same conditions ordinary rubber has frozen completely.

Anhydride rubber resembles crude rubber in the fact that a smooth homogeneous sheet can be obtained by simple calendering (see the left-hand sheet in Figure 5).

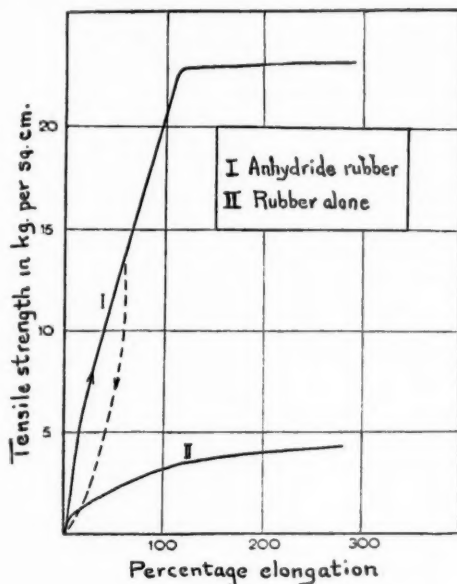


Fig. 6.—Stress-strain curves of samples shown in sheet form in Figure 5.

In brief, plasticized anhydride rubber is characterized by its elasticity under small deforming forces and by its plasticity under high deforming forces. In this respect it would appear to resemble certain synthetic rubbers which have been milled. Likewise tests by the present authors have shown that ordinary rubber-sulfur vulcanizates behave similarly if they are milled energetically for a very long time. This phenomenon will be studied more thoroughly later.

Heat does not alter appreciably the properties of anhydride rubber. It appears, however, if judged by the behavior of the crude and heated products, that heating has an effect, independent of, or complementary to, the main reaction. After heating for one-half hour at 143°C , for example, the product always swells a little less in benzene than it did before being heated, whatever the percentage of maleic anhydride and, if the reaction is complete, whether or not the product has been plasticized. Some data on this point are shown in the last column of Table 1.

It has been mentioned that maleic anhydride can be added to rubber under sufficiently mild conditions on a mill so that there is no reaction, and the milled product is completely soluble in benzene. On the contrary after this mixture is

heated, it no longer dissolves completely, and leaves a considerable proportion of gel. Consequently heating brings about at least some reaction.

In other experiments, maleic anhydride was added to rubber, not by mixing on a mill, but by imbibition, *e.g.*, by means of an ether solution. With unmilled rubber, subsequent heating does not induce any reaction, whereas it does lead to a reaction in rubber which has been previously milled. This would seem to indicate that there is formed during milling a product which catalyses the reaction between rubber and maleic anhydride.

VULCANIZATION OF ANHYDRIDE RUBBER

Since anhydride rubber can be vulcanized by sulfur, it seemed logical to hope that its tensile strength might be increased by this process, and that its resistance to solvents and its lack of thermoplasticity, both of which are characteristic of the original product, might also be improved. The practical side of this problem will be taken up later, and at the moment only some of the general features of vulcanization will be discussed. This general information should be considered chiefly as a basis for further work in the future, in which any improvements which may be made will depend to a great extent on the applications under consideration.

The product to be vulcanized contains the anhydride of a dibasic acid. Now it is well known that dibasic acids are retarding agents; therefore it is not surprising that vulcanizing mixtures containing this compound did not give good results. The vulcanizates which were obtained seemed to be undercured, and their tensile strengths reached only 50 kg. per sq. cm. (711 lbs. per sq. in.). The presence of uncombined maleic anhydride may have been responsible for these poor results. The attempt was therefore made to wash and then dry the reaction product before adding the vulcanizing agents, but this treatment gave hardly any improvement. This pointed to combined maleic anhydride itself as the cause of the bad quality. In an attempt to overcome this effect, polyhydroxy compounds were added, with particular attention to ethyleneglycol. These compounds gave appreciably better quality, but the best results were obtained by adding inorganic or organic bases at the same time that the vulcanizing agents were added. In this way satisfactory vulcanizates were obtained.

USE OF ORGANIC BASES AS NEUTRALIZING AGENTS

The mixture used in the study of vulcanization had the following composition:

Rubber	100
Sulfur	5
Mercaptobenzothiazole	1
Stearic acid	1
Zinc oxide	20

The control mixture, *i.e.*, the mixture prepared with ordinary rubber, when vulcanized for 15 minutes at 143° C, showed an elongation at rupture of 700 per cent and a tensile strength of 220 kg. per sq. cm. (3130 lbs. per sq. in.).

This particular recipe was chosen for the simple reason that, among the various recipes which were used in studying the vulcanizing properties of rubber-maleic anhydride mixtures, it was the one which gave the least bad results.

Among the basic neutralizing agents which were tested were the following, which are listed in the order of their decreasing activity: hexamethylenetetramine, *m*-phenylenediamine, aniline, *m*-toluylenediamine, *p*-phenylene-

diamine, benzidine, benzylamine, β,β' -dinaphthyl-*p*-phenylenediamine, and diphenylamine. The mixtures were vulcanized at 143°C in the form of moulded sheets 2 mm. thick, and in the form of calendered sheets 0.2 mm. thick in open steam. Different percentages of each neutralizing agent were tested. In a general way the best mechanical properties seemed to be obtained when the quantity of alkaline compound corresponded to that necessary to neutralize the maleic anhydride, *e.g.*, 5-7 parts of hexamethylenetetramine per 100 parts of rubber.

Great differences were found between the mechanical properties of the vulcanizates cured as sheets in open steam and those cured in a mould. The vulcanizates cured in open steam and containing hexamethylenetetramine, *m*-toluylenediamine, *p*-phenylenediamine and *m*-phenylenediamine, respectively, had tensile strengths of 180 to 200 kg. per sq. cm. (2560 to 2845 lbs. per sq. in.), *i.e.*, almost as high as the tensile strength of the control sample. The tensile strengths of the vulcanizates cured in a press hardly exceeded 130 kg. per sq. cm. (1849 lbs. per sq. in.). Both types of vulcanizates had elongations at rupture of about 300 per cent: These differences in tensile strength between the steam-cured and press-cured samples may be attributable to the tendency of the vulcanizates to tear, which is the greater the thicker the samples.

Some of the neutralizing agents which were tested have, as is already known, considerable activating effect on mercaptobenzothiazole. This is particularly true of hexamethylenetetramine, *m*-toluylenediamine, *p*-phenylenediamine and benzylamine, with which the time of vulcanization was reduced to 4 or 5 minutes. This very short time of vulcanization is a disadvantage because in such cases there is no appreciable plateau effect. Aniline, with which tensile strengths as high as 130 kg. per sq. cm. (1849 lbs. per sq. in.) were obtained, without its shortening the time of vulcanization below 10 minutes, is an exception to this rule. However, hexamethylenetetramine seemed to be of particular interest, for, contrary to the other alkaline compounds which were tested, it had a tendency to plasticize rather to stiffen the mixtures. Accordingly attempts were made to improve the mechanical properties of mixtures containing hexamethylenetetramine by changing various conditions. Particularly promising results were obtained in studies of the influence of the milling conditions during and after the reaction with the anhydride on the properties of the vulcanizates.

These tests, some results of which are given in Table 2, indicate that it is advantageous to operate with as high a friction ratio as possible, and to cool the rolls during the reaction, but to plasticize the product and to add compounding ingredients with the rolls slightly heated. There is a limit to what can be done in this respect because of the tendency of the products to stick to the rolls at elevated temperatures. But the rolls can be heated to 40° or 50° C quite satisfactorily. Under such conditions, strict control of the conditions during milling is indispensable for good reproducibility of results⁴.

In other tests the attempt was made to find mixtures in which the hexamethylenetetramine did not have the troublesome activating effect which it has with mercaptobenzothiazole. To this end mercaptobenzothiazole was replaced by alkaline accelerators and by derivatives of mercaptobenzothiazole. Although these experiments are still in progress, enough results have already been obtained to indicate that replacement of mercaptobenzothiazole in this way gives better vulcanization. But even with zinc pentamethylenedithiocarbamate, butyraldehydeaniline and diphenylguanidine, the best mechanical properties which have so far been obtained are still inferior to those obtained with mercaptobenzothiazole itself.

INORGANIC BASES

A few tests of inorganic bases were carried out. As a neutralizing agent, magnesia gave only mediocre results. On the contrary, litharge (10 per cent by weight) gave vulcanizates with tensile strengths of 120 to 130 kg. per sq. cm. (1707 to 1849 lbs. per sq. in.) in normal times of vulcanization. These mixtures have the disadvantage of sticking badly to any moulds which have not been carefully treated with a soap solution, a disadvantage which is all the worse because the vulcanizates are fragile when still hot.

PROPERTIES OF VULCANIZATES OF ANHYDRIDE RUBBER

Vulcanizates prepared from the product of the reaction of a mixture of 100 parts of rubber and 5 parts of maleic anhydride had elongations at rupture of 300 to 400 per cent and tensile strengths of 120 to 140 kg. per sq. cm. (1707 to 1991 lbs. per sq. in.), with rather high moduli. With increase in the percentage of maleic anhydride, the elongation at rupture and the tensile strength decreased, and the modulus increased.

The swelling of these products in solvents was considerably less than that of ordinary vulcanizates of the same type. For example, a vulcanizate prepared from a mixture of rubber and 5 per cent of maleic anhydride swelled in gasoline only about one-half as much as did a vulcanizate of the same composition but prepared from ordinary rubber. The further the reaction between rubber and maleic anhydride has been carried, i.e., the higher the percentage of combined maleic anhydride, the less does a particular type of vulcanizate swell in a solvent.

The thermoplasticity of both the raw and vulcanized mixtures of anhydride rubber is less marked than that of the corresponding mixtures of ordinary rubber. Applications based on this lower degree of thermoplasticity will be described later.

Judged by a few preliminary tests, the permeability to gases seems to be diminished by treatment of rubber with maleic anhydride.

The serious disadvantage of the vulcanizates so far studied is their poor resistance to tearing. Their stiffness is a disadvantage only to the extent that it restricts their applications to articles which need not be extremely flexible.

The aging properties have not been studied thoroughly, but tests in a Geer oven have indicated that anhydride rubber vulcanizates should age about as well as corresponding vulcanizates containing no maleic anhydride.

It will be evident from this brief survey that there is still much to be done to develop mixtures suitable for practical use. But because of the ease of processing and the new uses to which it may be put, anhydride rubber would seem to merit further attention. It is for these reasons that it has seemed advisable to publish the results so far obtained.

REFERENCES

- ¹ Le Bras, *Rev. gén. caoutchouc* **19**, 43 (1942).
- ² Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, **1938**, p. 256.
- ³ Compagnon and Le Bras, *Compt. rend.* **212**, 616 (1941); *Rev. gén. caoutchouc* **18**, 89 (1941).
- ⁴ An important variable is the amount of maleic anhydride which actually combines with the rubber. Since maleic anhydride is to a certain extent volatile, there is considerable loss during the reaction, e.g., when 5 per cent of maleic anhydride is added originally, the amount which finally remains after the rubber mixture has been heated during milling may be only 3.5-4 per cent. The properties of the vulcanizate depend on the proportion of maleic anhydride which combines with the rubber, so to obtain a uniform product it is necessary to carry out the reaction at all times under exactly the same conditions.

PRINCIPLES OF A METHOD OF VULCANIZATION BASED ON CONDENSATION REACTIONS. PROSTHESIS AND SYNESIS *

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GENERAL DISCUSSION

The term vulcanization was restricted originally to the treatment of rubber by sulfur at elevated temperatures, the purpose of which was to overcome the faults of the raw material and in general to make it of more practical value. For more than a half century, sulfur and a few sulfur compounds were the only agents known to have this remarkable property, but later selenium, tellurium, and finally various oxidizing agents and sulfurizing agents as well were found to be capable of vulcanizing rubber¹.

In all these transformations, the vulcanizing effect is the result of the direct or indirect action of one of the elements of the second group of metalloids.

On the assumption that vulcanization involves the formation of bridges between linear molecules², it was decided to attempt to bring about this bridge formation by classic condensation reactions under such conditions that it would be certain that elements of the second group of metalloids would play no part in the reaction.

The difficulty in uniting rubber hydrocarbon chains lies in their lack of reactivity, for their structure is of such a character that it is not easy to bring about a double linking reaction by condensation through an intermediate agent. It was attempted to overcome this difficulty by first adding active nuclei to the hydrocarbon chains. With this accomplished, it remained as a second step only to join together two active centers by a suitable chemical reagent; a process which should, if the scheme turned out to be correct, result in vulcanization.

We have, then, to consider a form of vulcanization which involves two successive phases. The active nuclei fixed on the hydrocarbon chains can be regarded as "prosthetic" groups, in conformity to the meaning of this term in organic chemistry. Accordingly the chemical process by which prosthetic nuclei are fixed on the chains will be designated as *prosthesis*, and the union of prosthetic nuclei by means of a suitable reagent will be designated as *synesis*.

The combined process of prosthesis and synesis can then be represented

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schematically in the following way:

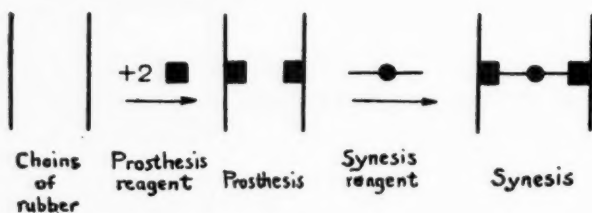


FIG. 1.

Account must also be taken of the fact that the prosthetic agent, since it is capable of attaching itself to a chain, can likewise attach itself to two chains at the same time. In this case the prosthesis reagent and the synesis reagent become a single reagent with a dual function, as shown in the following scheme:

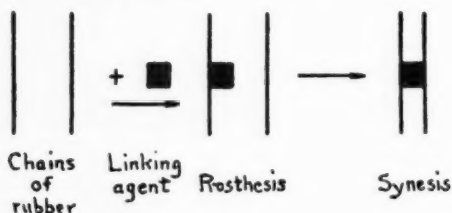


FIG. 2.

For this process to give soft vulcanized rubber, the condensation reactions must take place only at a few points in the molecules. If the resulting tridimensional network is too compact, that is, if bridges are formed between too many double bonds, the product is hard and brittle and resembles ebonite formed by vulcanization with sulfur.

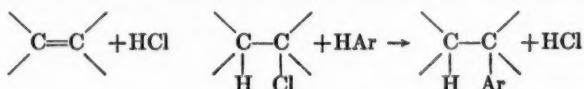
In the present work, the purpose of which was to settle a theoretical point, it was not so much a matter of obtaining a commercially useful material as it was of carrying out certain well defined reactions which could be easily interpreted. Contrary to ordinary chemical reactions, there was in this case no means available for extracting and identifying the products which were formed and any data obtained had to be obtained by indirect methods. Reasons such as this governed the choice of reagents and the technique which was employed, without regard to the quality of the products obtained. The application of the results and of the data to practical ends is the subject of work now in progress.

The condensation of formaldehyde with phenols was chosen as typical of a synesis reaction. In this case the phenol acts as the prosthetic agent, thus:

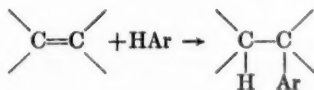


where Ar represents the phenol. The prosthetic reaction of the phenol is the most difficult in the whole process to carry out. For the phenol to unite with rubber, an energetic type of reaction and at the same time an energetic reagent must be chosen in order to overcome the low reactivity of the rubber hydrocarbon. It was decided to resort to a condensation of the Friedel-Crafts type, induced by hydrogen chloride, with resorcinol, the reactivity of which is well known. The reaction with hydrogen chloride may proceed in two ways, each

of which leads to the same final result: (1) initial addition to the double bonds, followed by condensation of the intermediate chlorinated compound, thus:

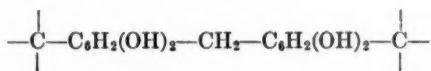


or alternatively, (2) the catalytic addition of the aromatic molecule to the double bond, thus:



This is nothing but the addition, so often described, of phenols to unsaturated hydrocarbons, *e.g.*, to isoamylene and styrene³.

In brief, the process leads to the formation of methylenediaryl linking groups between the rubber chains:



The application of this process has given products which have the essential characteristics of ordinary vulcanized rubber, so these prosthesis-synthesis reactions may be regarded as representative of vulcanization reactions⁴.

It should be evident, however, that, because of the chemical difference between sulfur bridges and the bridges represented above, the properties of these vulcanizates will be different in various respects from those of sulfur vulcanizates.

The interaction of rubber, hydrogen chloride and resorcinol or, in a more general way, of rubber, hydrogen chloride and a phenol, has already been described in the literature. The reader is referred, for example, to the numerous patents of Fisher⁵, which described both hard and thermoplastic transformation products, which are formed by reactions carried to a much further point than those in the present work⁶. The previous investigators applied these reactions to rubber with the particular purpose of obtaining useful resins, and they did not make a thorough study of the chemical reactions which are responsible for the effects. For lack of any definite knowledge as to their character, these chemical changes in rubber have been designated by the term "isomerization". However, in view of the uncertain knowledge of the subject, this is too precise a meaning of the phenomenon.

It might be well also to recall the action of phenols on brominated rubber. This reaction was first reported by Weber⁷, was later confirmed and extended by Fisher, Gray and McCollm⁸, and Geiger⁹, and most recently has been described by Low¹⁰, who applied the reaction to chlorinated rubber. In these cases a Friedel-Crafts reaction, catalyzed by metal chlorides, is involved. The product obtained is completely saturated, and is an amorphous powder soluble in acetone and in alkaline solutions.

With reference to previous work on synthesis reactions, there is no reason for discussing experiments carried out with the purpose of forming phenol-formaldehyde resins *in situ* in rubber, because both the principles involved and the products obtained are very different from those concerned in the work described

in the present paper. Only a patent recently taken out by the Dutch Rubber Stichting will be cited¹¹, for according to this patent certain so-called "active" phenol-formaldehyde resins have a true vulcanizing action¹². On the other hand, in the process developed in the present work, the resins which may be formed by the synesis reaction are, as will be described later, without any appreciable vulcanizing action.

Finally in concluding this rapid survey of previous related work, it is well to call attention to the fact that Kirchhof has reported that formaldehyde reacts with rubber which has previously been modified by treatment with sulfuric acid¹³, with formation of a powdery substance. There is also a patent on the action of formaldehyde on rubber in the form of acidic, stabilized latex¹⁴, with a view to improving the quality of the coagulum.

PROSTHESIS

The prosthetic reaction, as has just been seen, involves condensation of a phenol induced by an acid; in the case described the phenol was resorcinol, the acid hydrogen chloride.

At first hydrogen chloride was used in the gaseous state, and in a few experiments it was made to react at elevated temperature on a mixture of rubber and resorcinol. Later it was found more convenient to combine the acid and rubber separately¹⁵.

A priori it would appear to be important whether this hydrochlorination is carried out on a part or on the whole mass of rubber. In the first case hydrogen chloride molecules accumulate on the same hydrocarbon chain, whereas in the second case they are distributed over a large number of chains. Consequently for a given percentage of hydrogen chloride in the final mixture, there will be either polychlorinated filaments enveloped by molecules containing no chlorine or molecules which have been chlorinated by the laws of chance, *i.e.*, if not uniformly so, at least without extreme differences in concentration and deficiency.

Suppose, for example, that 5 per cent of hydrogen chloride is to be added. This can be done by adding to a portion of the crude rubber 22.3 per cent of 26 per cent hydrochloride (75 per cent of the double bonds of which have accordingly been saturated with hydrogen chloride). In this way there is obtained a mixture containing 85.8 per cent of intact chains, *i.e.*, theoretically inert so far as the prosthetic reaction is concerned, whereas uniform hydrochlorination to the same percentage would mean one chlorine atom for about every ten double bonds. Consequently great differences between the two types of mixtures would be expected, for in the first type the reaction is localized on a limited number of molecules, instead of all molecules taking part in the reaction, as in the second case.

Now it has been found experimentally that quite the contrary is true, *viz.*, that it makes very little difference how the hydrogen chloride is added, provided only that the hydrochloride is not in such a physical state that difficulty is encountered in obtaining a homogeneous mixture. Such a difficulty is avoided when the hydrochlorination is below 25-26 per cent; above this proportion miscibility with crude rubber is very imperfect, and "clots" remain disseminated throughout the mass. This incompatibility becomes more pronounced as the theoretical limit of 34.9 per cent of hydrogen chloride is approached.

It can only be concluded from this that the original position of the chlorine plays no part in the condensation process, and consequently that the active agent is a mobile form of hydrogen chloride formed by simple solution or even slight dissociation of the hydrochloride. A very small number of these free molecules is sufficient, whatever the mechanism of condensation, since they are regenerated continuously. It would seem, moreover, that the number of "effective" reactions does not need to be very great to bring about a marked effect of vulcanization, as has already been suspected of vulcanization by sulfur¹⁶, and as would be expected in view of the theory of filiform molecules of Staudinger.

In view of all this, rubber hydrochloride must be regarded merely as a "donor" of hydrogen chloride.

With this point settled, the remaining problem was to make resorcinol react after it had been incorporated in the rubber mixture. This operation was carried out at an elevated temperature, with four factors varied, *viz.*: the percentage of resorcinol, the percentage of hydrogen chloride, the temperature, and the time of heating. When each of these four factors is increased gradually while the other three factors are maintained constant, a series of phenomena is observed in most cases. First of all, under the mildest conditions the samples which have changed to the point that they keep their shape after removal from the mould are rather tacky, are very stretchy, have a high permanent set, are fragile, and swell greatly (though they are little soluble in solvents). These are the properties which are obtained, for instance, when a mixture containing 20 per cent of resorcinol and 1 per cent of hydrogen chloride is heated for 180 minutes at 143° C. The surface becomes less tacky, the tensile strength and extensibility increase and the permanent set remains at 50–200 per cent (when stretching is rapid), so that the substance finally obtained appears to be quite similar to leather. Finally this leatherlike substance becomes less and less flexible, and the ultimate product is a true ebonite which is hard and brittle. The most advanced state is that which has been described by Fisher⁷.

The products obtained when the conditions of the reaction are relatively mild can be readily milled; on the contrary, the products which resemble leather are changed by milling into powders which are difficult to plasticize. In all cases the products are more flexible when hot than when cold.

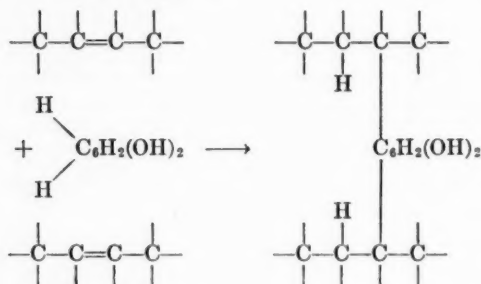
The threshold of the reaction, as well as its completion, for each of the factors considered depends on the values of the other factors. If these values are very low, the last stage is never reached. This is the case, for example, with a mixture containing 1 per cent of hydrogen chloride and 5 per cent of resorcinol, which never reaches the ebonite state.

The greater part of the resorcinol does not enter into the reaction, and the less the rubber is modified the greater is the proportion remaining free. In one of the normal samples, for example, it was found that only one-fifth of the resorcinol had entered into combination. On the other hand part of this reagent condenses with itself under the influence of hydrogen chloride, with formation of triresorcinol hydrochloride¹⁸, which imparts to the mixture a characteristic red color.

It is evident from the properties of the various products which were obtained that those which were formed under the mildest conditions resemble raw rubber, while those in more advanced stages are, with their slight plasticity, more nearly like vulcanized rubber. This similarity may be the result of a double condensation reaction between resorcinol and the rubber chains in

accordance with the scheme shown in Figure 2. This is a reaction which would prevail under the most energetic conditions.

The reaction might be, for example:



This reaction seems very probable in view of the investigations of Koenigs and Mai¹⁹ on the mutual reaction of resorcinol with isoamylene in the presence of sulfuric acid which leads to the condensation of one molecule of resorcinol with 2 molecules of isoamylene.

Further tests were carried out to determine the influence on the rubber-resorcinol-hydrogen chloride reaction of ordinary catalysts of this type of condensation. It was found that small amounts of zinc chloride, formed *in situ* from zinc oxide, had a very marked effect; only 0.5 per cent of zinc oxide was sufficient to carry the reaction to the same point under the mildest conditions. It would seem that this catalytic effect should make it possible, by the use of lower temperatures, *e.g.*, 100–110° C instead of 140° C, to promote the prosthetic reaction without at the same time promoting the double condensation reaction already discussed, so that the final product can be milled more easily.

SYNESIS

The reaction which it was assumed would take place as a second step in the process was the union, by means of formaldehyde, of the molecular chains of rubber carrying molecules of resorcinol.

Trioxymethylene or paraformaldehyde²⁰ was added to a prosthetic mixture which had not reacted sufficiently to be difficult to mill, *e.g.*, the product obtained by heating a mixture of rubber 100 parts, resorcinol 20 parts, and hydrogen chloride 5 parts, for 2 hours at 110° C. The hydrogen chloride in the prosthetic mixture brings about the condensation with the resorcinol nuclei. It was found that, by heating for a short time at ordinary vulcanizing temperatures, the high permanent set and the thermoplasticity of the prosthetic mixture disappeared; the samples became nery, elastic and insoluble. In view of this they can be regarded indisputably as vulcanized rubber. Another very important indication of the change which takes place in rubber under these conditions is the considerable decrease in its affinity toward solvents; *e.g.*, a prosthetic mixture which swelled 620 per cent in benzene gave, after synthesis, a product which swelled only 200 per cent.

In general, vulcanizates obtained by this method, are less extensible (100 to 200 per cent at rupture) and are harder than sulfur vulcanizates; also they swell less in solvents than do sulfur vulcanizates. The tensile strength is

never high, *i.e.*, it lies between 500 and 1000 grams per sq. mm. (715 to 1430 lbs. per sq. in.).

Obviously the resorcinol which remains uncombined after the prosthetic reaction is completed reacts with part of the formaldehyde, with formation of a resin which is, in virtue of its formation under these conditions, perfectly dispersed in the reaction mixture. With small additions of formaldehyde (2 per cent) there is no appreciable synesis, and in this case the little formaldehyde which is added is taken up completely by the free resorcinol. This happens likewise when rubber, hydrogen chloride, resorcinol and formaldehyde are made to react simultaneously without any preliminary prosthetic reaction. This is justification for carrying out the process in two steps, and shows in addition that the resins formed *insitu* are not responsible for the transformations which take place.

To prove this still more conclusively, prosthetic mixtures were made to undergo synesis after all free resorcinol had been removed. The resorcinol was removed by extraction, after which the product was dried and then synesized. In this case the synesis reaction not only progressed smoothly, but more easily, for the addition of small percentages of formaldehyde, *e.g.*, 2 per cent, carried the transformation to an advanced stage.

The products obtained by this process are characterized by a transparency similar to that of certain sulfur vulcanizates, a property which is good evidence of their homogeneity. Their tensile strengths and swelling in solvents are of the same orders of magnitude as those of the products obtained by synesis with the same proportions of formaldehyde, of corresponding prosthetic mixtures which have not been previously extracted by acetone. The fact that the swelling properties are the same as the best proof that the reaction is the same in the two cases. The resorcinol-formaldehyde resin which is formed is not, therefore, the cause of vulcanization²¹.

With respect to prosthesis, the influence of various factors in the reaction on the properties of the final product were studied. The experiments show that the best means of changing systematically the properties of the synesis product is through the agency of the prosthetic reaction. The greater the extent to which the latter reaction has been carried, the more closely do the properties of the final product approach those of ebonite; swelling and elasticity diminish progressively while the tensile strength increases.

Below a certain point, the percentage of formaldehyde in a given prosthetic mixture is of particularly great influence. This critical percentage probably corresponds to the quantity of formaldehyde required by the resorcinol in its combined and free forms. Above this percentage, however, there are still changes, although relatively small, in the properties of the vulcanizates, *e.g.*, an increase in the tensile strength and a decrease in swelling and extensibility. The reasons for these changes will be discussed later.

The effect of heating is very pronounced, but is of limited duration, and varies with the temperature. The synesis reaction takes place even at room temperature, but in this case requires several days. At elevated temperatures, the reaction is rapid; at 80° C it is complete in 30 minutes, and above 150° C it is complete in a few minutes. But after the reaction is completed, the properties of the material no longer change when the heating is prolonged, and no phenomena comparable to those of overvulcanization are observed, *i.e.*, the plateau effect is indefinitely long. For example, around 185° C, it is immaterial whether the heating is for only a few moments or for a half hour.

OTHER REACTIONS OF PROSTHESIS-SYNESIS

The complex rubber-resorcinol-formaldehyde-resorcinol-rubber has been presented as a typical model of an intermolecular bridge, the formation of which constitutes true vulcanization. But, as has been indicated in the general discussion, every reaction which involves a double union must lead ultimately to a similar effect whenever this union takes place between two molecules of rubber. It is the properties of the vulcanizates alone which vary according to the agents used.

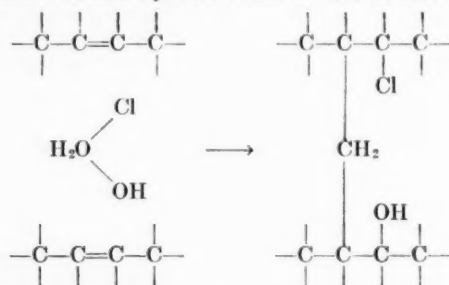
The number and the variety of such reactions are unlimited, and we shall limit ourselves to two, which are related to the present work, *viz.*, vulcanization by resorcinol and by formaldehyde, in each case the reagent being used alone.

Prosthesis-synesis with resorcinol but no formaldehyde.—The principle and also the effects obtained have already been pointed out. When the reaction is carried far enough, prosthesis with resorcinol has all the characteristics of vulcanization, an effect which must be attributed to a double union of a resorcinol molecule to rubber chains. However, the resulting product has poor mechanical properties.

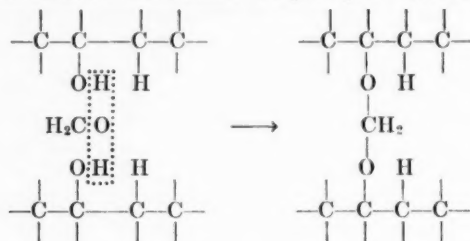
Prosthesis-synesis with formaldehyde but no resorcinol.—In view of the well-known properties of formaldehyde, it is easy to conceive of a reaction involving double union to the ethylenic chains. Like other aldehydes, formaldehyde is the anhydride of a diol, *viz.*, $\text{H}_2\text{C}(\text{OH})_2$, and in virtue of this, it reacts in many cases as if it had a dual functional capacity, making it capable of forming a linking between two hydrocarbon chains.

Three normal reactions are shown below, in all three of which hydrogen chloride plays an intervening part, with or without the formation of the intermediate addition product $\text{H}_2\text{C}(\text{OH})\text{Cl}$, *i.e.*, the monohydrochloride ester of the diol.

(1) Simple addition of this hydrochloride to the double bonds:

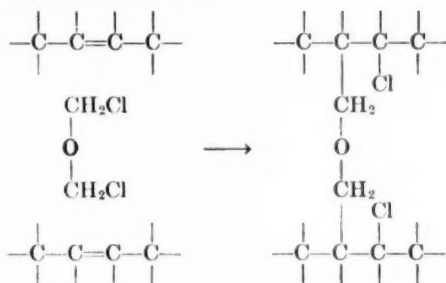


(2) Reaction of the hydrated product resulting from the double linking either with the formaldehyde hydrochloride or, what amounts to the same, with formaldehyde itself under the influence of hydrogen chloride.



This hydration can take place through the agency of water which is inevitably present, either by direct addition catalyzed by hydrogen chloride or by partial hydrolysis of rubber hydrochloride.

(3) Addition of the dichloromethyl ether $(\text{ClH}_2\text{C})_2\text{O}$, formed by the action of hydrogen chloride on formaldehyde:



An example of this kind of addition reaction is the union of dichloromethyl ether with propylene²², with formation of dichlorodibutyl ether according to a scheme corresponding exactly to that shown for rubber.

These various reactions, and others besides, are theoretically possible, but they certainly must take place less easily than the condensation of formaldehyde on the resorcinol nucleus. It is not surprising then that vulcanization by formaldehyde in the absence of resorcinol is more difficult. Vulcanization can, however, be accomplished by the addition of hydrogen chloride, *e.g.*, 1 per cent, to the mixture. In this way it is possible to obtain with 10 per cent of formaldehyde, a supple, elastic material without high permanent set, and which does not swell in solvents as do sulfur vulcanizates.

The two possible types of prosthesis-synthesis reactions with each of the two reagents used separately are of particular interest in showing the very general nature of the vulcanization process.

The experiments which have been described are also of help in explaining the chemical mechanism involved in the mixed vulcanization with resorcinol and formaldehyde. They show, for example, that the independent action of each of these two reagents plays only a very small part in the vulcanization process. This is evident merely by comparing the properties of the three types of vulcanizates.

But above all else the operating conditions best distinguish the three processes. Synthesis is incomparably more rapid in the mixed reaction than in the separate reactions with the individual reagents. This is particularly true of the reaction with formaldehyde alone, as shown not only by previous evidence but by the data in Figure 3, which shows a prosthetic rubber-resorcinol mixture to which formaldehyde was added and which was then stored at room temperature without having been heated at all.

It is evident that, after twenty days at room temperature, the prosthetic rubber-resorcinol to which formaldehyde was added swelled hardly any more in benzene and in gasoline than it would have done if it had first been heated 15 minutes at 143°C . On the contrary a rubber hydrochloride-formaldehyde mixture showed no decrease in solubility even after several months, and at room temperature the synthesis reaction with formaldehyde alone was practically negligible.

The best way to explain why rubber molecules become more sensitive to the action of formaldehyde after they have reacted with resorcinol by prosthesis is that they have combined with this particular phenol and that formaldehyde then reacts with the resorcinol nucleus. This does not exclude in any way a further direct fixation on the carbon chains, particularly when the proportion of formaldehyde is greater than that necessary for combination with all of the free and combined resorcinol.

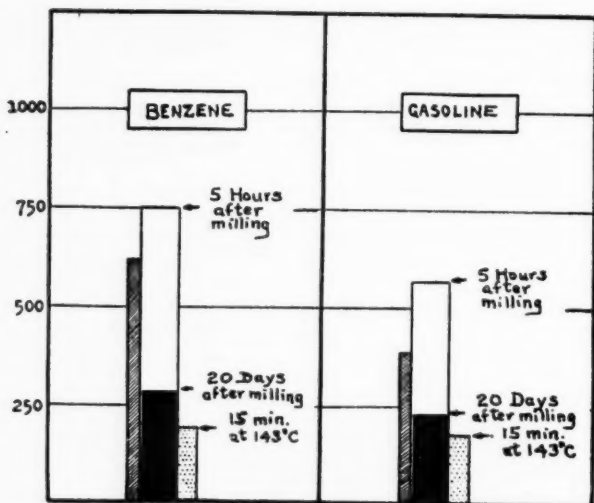


Fig. 3.—Action of formaldehyde on a prosthetic mixture at room temperature.

The cross-hatched columns show the swelling of the prosthetic mixture.

The white and black columns show the swelling of the prosthetic mixtures, after milling with 10 per cent of formaldehyde, and after resting for different lengths of time.

The dotted columns show the swelling of the control mixture which has been subjected to the synesis reaction at elevated temperature.

In any case, one seems justified in disregarding any vulcanizing effect of oxygen or of any other oxidizing agent, since the transformation takes place only under the normal conditions of condensation reactions, which are known not to involve any intermediate action of oxygen.

In view of this, the mechanism of vulcanization by the successive action of resorcinol and formaldehyde is in all probability that which has already been suggested, *viz.*, prosthesis, involving combination of rubber and resorcinol, and synesis, involving the formation of the complex, rubber-resorcinol-formaldehyde-resorcinol-rubber, to which is due the vulcanizing effect.

CONCLUSIONS

It follows from the investigation which has just been described that, in accordance with predictions, rubber can be vulcanized by simple classic condensation reactions. Admittedly the crude products prepared in this way are not of sufficiently good quality to be of direct use as such. In particular they deteriorate very rapidly; vulcanizates prepared from rubber-resorcinol-formaldehyde mixtures harden and lose their elasticity in the course of several weeks, and vulcanizates prepared from rubber-formaldehyde mixtures deteriorate still more rapidly.

However, this shortcoming and other less serious ones are of only secondary importance compared to the principle in question, particularly since it is to be hoped that these faults can be overcome, either by suitable corrective measures or, more important, by further developments in the method.

Experiments have already been carried out with these aims in view, and acidic compounds other than hydrogen chloride, aromatic compounds other than resorcinol, and linking agents other than formaldehyde have been studied.

Vulcanization by formaldehyde alone suggests that there are vulcanizing reactions entirely different from condensations on aromatic nuclei; for example, among many possibilities, there is the double addition to the ethylenic linkages of diacids attached at their extremities by two ester groups. In this way it should be possible to extend at will the linkages which unite filiform molecules of rubber, and supposedly this free play in linking molecules would lead to the development of interesting mechanical properties.

Since a vulcanizing effect is obtained by uniting rubber chains by a condensation reaction, the question arises whether other forms of vulcanization can be explained in the same way. This is probably the case in the interesting process of Fisher²³, who used aromatic compounds as reagents, among them phenols, with the further aid of an oxidizing agent. Now oxidation is, as is well known, one of the accepted means of uniting an aliphatic carbon to a nucleus; for example, this method is largely used in the manufacture of triphenylmethane dyes. The oxidizing agent unites the aromatic nucleus simultaneously to two carbon atoms of the rubber chains.

Since in all probability ordinary vulcanization by sulfur depends on the agglutination of hydrocarbon chains, all the methods involve fundamentally the same general mechanism.

The new methods have, however, the advantage of greatly enlarging the present-day technical field. But, in common with older methods, they have the disadvantage of a random action on the rubber molecules, in that the intermolecular linkings which are formed are distributed at random along the hydrocarbon chains. It would be extraordinary if under these conditions the structure most favorable to good mechanical properties were to be formed. The next investigations should be directed not only to linking chemically the chains to one another but also the correct choice of location of these linkings by suitable control of the vulcanizing reactions.

EXPERIMENTAL PART

In what follows, swelling is expressed as the percentage increase in volume, based on the original volume. It was measured by the volumetric method used and discussed by Dufraisse and Velluz²⁴. The tensile strength and extensibility were measured on a Scott inclined-plane machine.

Preparation of rubber hydrochloride.—The method followed was that described by Oenslager²⁵. Ethyl acetate was saturated with hydrogen chloride, i.e., so that it contained 16–17 per cent. In this solution a thin sheet of slightly masticated crepe rubber was immersed until 100 grams had taken up 25 per cent of hydrogen chloride, a process which required about three-quarters of an hour. After immersion the ethyl acetate which also had been absorbed was removed by placing the sample in a desiccator in a vacuum over sodium hydroxide to absorb at the same time any uncombined hydrogen chloride. The rubber hydrochloride was finally homogenized by milling.

Determination of the hydrogen chloride content.—After having proved that

rubber hydrochloride loses all of its chlorine in the form of hydrogen chloride when heated, the following method was used for determining the hydrogen chloride content of rubber hydrochloride.

In a Pyrex tube of 50 cc. capacity are placed 0.250 gram of rubber hydrochloride and 2 grams of calcium oxide so that they cover completely the rubber hydrochloride; the tube is heated until red in a Bunsen flame, is then cooled, the residue is treated with dilute nitric acid (50-100 cc. of acid diluted to one-fifth its strength) and ethyl ether (10-20 cc.), and the chlorides in the solution are determined by the Charpentier-Vollard method.

Several analyses of the same rubber hydrochloride gave results which did not differ by more than 1 per cent from one another. As an example, the percentages of hydrogen chloride obtained by the analysis of one particular sample of rubber hydrochloride were 26.12, 26.12, 26.25 and 26.04. The good agreement in these results indicates that decomposition takes place smoothly and that no hydrogen chloride is lost in the analysis.

STUDY OF PROSTHESIS

MODE OF OPERATION

Addition of hydrogen chloride in the gaseous form (preliminary tests).—The samples of rubber to which resorcinol had been added by milling or by imbibition were heated in sealed tubes containing dry hydrogen chloride.

Addition of hydrogen chloride in the form of rubber hydrochloride.—Rubber hydrochloride and virgin rubber were mixed in proportions which gave the percentage of hydrochloride desired; the resorcinol was then added in the same way, and the mixture was heated in a mould in the conventional way.

Influence of the distribution of hydrogen chloride on the rubber chains.—A comparison was made of the products obtained from mixtures containing rubber 100 parts, hydrogen chloride 4 parts and resorcinol 20 parts, prepared from rubber hydrochloride containing: (1) 5 per cent of hydrogen chloride, and (2) 25 per cent of hydrogen chloride.

After heating for 3 hours at 140° C, the properties of the products obtained were those shown in Table 1.

TABLE 1

Product made by starting with rubber hydrochloride containing	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)	Swelling in benzene (percentage by volume)
5% hydrogen chloride	700	350	400
25% hydrogen chloride	830	300	375

The results, particularly the swelling values, agree sufficiently well to warrant the conclusion that the reaction is the same in the two cases.

All the tests described below were made with rubber hydrochloride containing approximately 25 per cent of hydrogen chloride.

STUDY OF DIFFERENT FACTORS IN THE REACTION

Influence of increasing proportions of hydrogen chloride.—In all the tests shown in Table 2, heating was for 3 hours at 140° C. To characterize the reaction products, the swelling values were chosen as the preferable criterion; the other properties were rather difficult to evaluate, particularly in the extreme cases, where the reaction had either progressed insufficiently or was too far advanced.

In a general way, the smaller the percentage of resorcinol, the less the effect of any particular increase in the proportion of hydrogen chloride.

TABLE 2

Resorcinol (percentage based on the rubber)	Hydrogen chloride (percentage based on the rubber)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)	Aspect
20	1	1325	—	—	—
20	2	950	200	—	—
20	2.5	500	320	—	—
20	3	450	—	—	—
20	3.5	425	750	—	—
20	4	375	830	300	—
20	4.5	300	—	—	Leathery
20	5	275	—	—	Leathery
20	10	225	—	—	Ebonite
20	25	—	—	—	Ebonite
10	1	dissolved	—	—	—
10	4	950	300	750	—
10	6	575	400	400	—
10	7	375	450	350	—
10	7.5	350	710	300	—
10	8	325	1130	—	Leathery
5	1	dissolved	—	—	—
5	4	1500	—	—	—
5	8	1375	—	—	—
5	12	1300	—	—	—
5	16	1000	—	—	—
5	26	275	—	—	Ebonite

Influence of increasing proportions of resorcinol.—The heating process was the same as before, viz., 3 hours at 140° C. The hydrogen chloride content was 4 per cent in all cases (see Table 3). The addition of increasing proportions of resorcinol had an effect similar to that obtained by the addition of increasing proportions of hydrogen chloride.

TABLE 3

Resorcinol (percentage based on the rubber)	Hydrogen chloride (percentage based on the rubber)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)	Aspect
5	4	1500	—	—	—
10	4	950	330	750	—
15	4	525	550	450	—
20	4	300	880	250	—
30	4	225	—	—	Ebonite
40	4	—	—	—	Ebonite

Influence of temperature.—The effects of temperature on the following three mixtures were studied:

Ingredient	A	B	C
Rubber	100	100	100
Hydrogen chloride	2	4	7.5
Resorcinol	40	20	10

The time of heating (3 hours) was the same in all cases (see Table 4).

TABLE 4

Mixture	Temperature (Centigrade)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)	Aspx.
A	120°	625	150	550	—
B	120°	625	450	500	—
C	120°	650	500	500	—
A	140°	450	350	450	—
B	140°	350	1300	250	—
C	140°	400	750	300	—
A	160°	—	—	—	Tough, leathery
B	160°	—	—	—	Ebonite
C	160°	—	—	—	Tough, leathery

Influence of the time of heating.—The same mixture was used throughout, and it was heated at 110° C and at 145° C for different times (see Table 5). This mixture contained 20 parts of resorcinol and 5 parts of hydrogen chloride per 100 parts of rubber.

TABLE 5

Time of heating (hours)	Temperature (Centigrade)	Swelling in benzene (percentage by volume)	Benzene extract (percentage of original volume)	True swelling (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
0.5	145°	910	12.3	1030	290	480
1	145°	400	2.2	408	430	260
2	145°	225	1.7	230	894	10
3	145°	Ebonite	—	—	—	—
1	110°	750	20	935	360	500
2	110°	620	13.7	720	400	470
3	110°	590	12.6	678	407	390

The data in Table 5 indicate that the higher the temperature, the greater is the influence of the time of heating.

Table 5 shows also benzene extracts which were determined at the same time as the swelling measurements. By allowing for this swelling effect, it was possible to calculate the true swelling, *i.e.*, the swelling as a percentage of the original volume minus the volume of rubber passed into solution. It is evident that partial solution of the rubber from the products obtained by short times of heating at 145° C decreases toward zero with increase in the time of heating, whereas partial solution of the rubber in products heated at 110° C is considerably even after prolonged heating.

The products obtained by heating at 110° C are characterized by their greater capability of undergoing synesis, in that they can be much more easily milled and plasticized than can those obtained by heating at 145° C.

Catalytic action of zinc oxide.—Prosthetic products in the most advanced stage, prepared by heating at 110° C with zinc oxide present, have the advantage of being much more readily masticated than corresponding mixtures containing no zinc oxide. This is evident from the results in Table 6, which gives data on a base mixture composed of 100 parts of rubber, 20 parts of resorcinol and 5 parts of hydrogen chloride, to which was added 0, 0.5 and 2 parts of zinc oxide per 100 parts of rubber. Each mixture was heated for 2 hours at 110° C.

This study of the various factors involved in the reaction shows that even the slightest change in any of the factors has a pronounced effect, as a result of which it is difficult to duplicate results on a given sample, especially at elevated temperatures.

TABLE 6

Zinc oxide (percentage, based on the rubber)	Swelling in benzene (percentage by volume)	Swelling in gasoline (percentage by volume)
0	620	380
0.5	435	290
2	Ebonite	Ebonite

DETERMINATION OF UNCOMBINED RESORCINOL

Not all the resorcinol enters into the reaction and, as happens in the case of sulfur in ordinary vulcanization, crystals of resorcinol soon appear on the surface of the vulcanized sample.

Attempts were made to determine the residual resorcinol so as to know, by difference, the maximum quantity which reacted with the rubber. The values obtained in this way must actually be these maximum proportions, because resorcinol tends to condense on the impurities in the rubber and also on itself. It is known, for example, that under the very same conditions used in the present work, triresorcinol hydrochloride is formed, which can be easily identified by its color, by its solubility in water, by the fluorescence of its sodium salt, etc.

To determine the quantity of free resorcinol in a sample, the latter was extracted for a long time by acetone, and the resorcinol in the acetone extract was then determined by bromine according to the method of Pence²⁶.

As an example, it was found that, after vulcanization for 1 hour at 110° C, a mixture of rubber 100, resorcinol 20, and hydrogen chloride 5, contained approximately 82 per cent of its resorcinol in still uncombined form. The order of magnitude of this value, as determined by chemical analysis, was confirmed by physical means, *viz.*, by determining the resorcinol in the acetone extract by the spectrographic method described by Dufraisse and Houpillart²⁷.

These determinations cannot be regarded as very precise, but their general order of magnitude can be relied upon. They show that the proportion of resorcinol combined with the rubber is certainly small in spite of the high proportions added to the rubber.

STUDY OF SYNESIS

OPERATING PROCEDURE

The prosthetic mixture was plasticized on a mill, and formaldehyde was added in the form of trioxymethylene or paraformaldehyde. The plasticized product was vulcanized in a mould in the ordinary way.

STUDY OF DIFFERENT FACTORS IN THE REACTION

Influence of the degree of prosthesis.—In a study of the prosthesis reaction a mixture (MP) composed of rubber 100 parts, resorcinol 20 parts, and hydrogen chloride 5 parts, was tested under the conditions shown in Table 6. Synesis was carried out with the addition of 10 parts of trioxymethylene per 100 parts of rubber. The swelling values in benzene, like those of the tensile strength,

show the marked influence of the degree of prosthesis on the product of synthesis (see Table 7).

TABLE 7

Mixture	Prosthesis		Synthesis (2 hours at 140° C)		Properties	
	Time of heating (hours)	Temperature (° C)	Formaldehyde (per 100 parts of rubber)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
MP	1	80°	10	350	350	150
MP	1	105°	10	275	540	280
MP	1	120°	10	200	550	150
MP	2	110°	10	200	750	130
MP + 0.5% ZnO	2	110°	10	120	1020	70

Influence of increasing proportions of formaldehyde (see Table 8).—The synthesis reactions were carried out with proportions of formaldehyde from 0 to 20 per cent (based on the rubber) in the following three prosthetic mixtures:

MP ₁	Rubber	100	heated 2 hours at 110° C
	Resorcinol	20	
	Hydrogen chloride	5	
MP ₂	Rubber	100	heated 2 hours at 110° C
	Resorcinol	20	
	Hydrogen chloride	5	
	Zinc oxide	0.5	
MP ₂ extracted	Same as MP ₂ but subsequently extracted by acetone to remove all uncombined resorcinol		

The values of the swelling in benzene and the tensile strengths are shown in Figures 4 and 5. These graphs make evident the fact already pointed out in the theoretical discussion, *viz.*, that the addition of small proportions of formaldehyde brings about synthesis only if the resorcinol has been eliminated from the

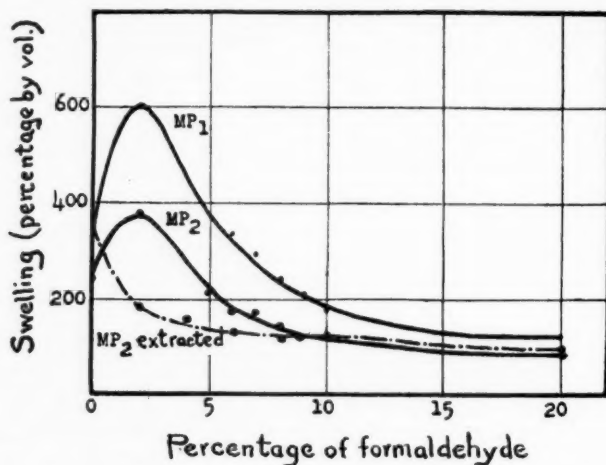


FIG. 4.—Effect of increasing quantities of formaldehyde on the swelling of the synthesis products in benzene.

mixture. It will be noted that, in general, the prosthetic mixture which has been extracted by acetone undergoes the synesis reaction just as well as, or even better than, the prosthetic mixture which has not been extracted, *i.e.*, which still contains free resorcinol. This proves conclusively that the resins formed by the action of formaldehyde on the uncombined resorcinol play no part in the phenomena which have been described.

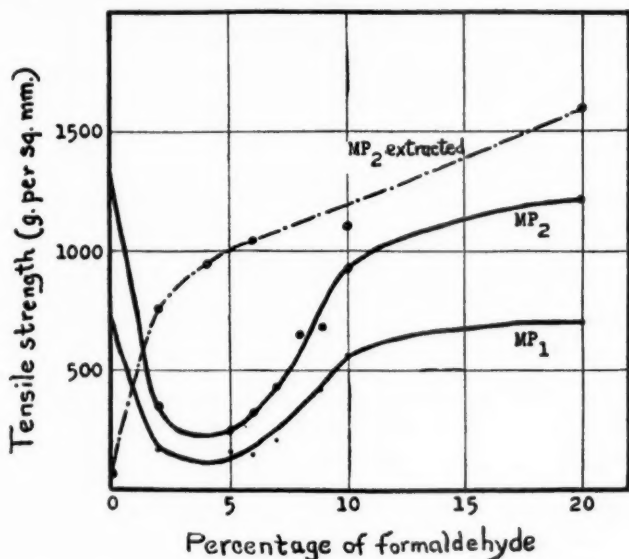


FIG. 5.—Effect of increasing quantities of formaldehyde on the tensile strength of the synesis products

Study of the plateau of vulcanization.—Even in the first experiments it became evident that, after a certain length of time, which depended on the temperature, the time of heating was without influence on the results. The data in Table 9 represent synesis reactions effected with 10 per cent of trioxymethylene in a prosthetic mixture composed of rubber 100, resorcinol 20, hydrogen chloride 5, and zinc oxide 0.5, which was heated for 2 hours at 110° C. These data show the extent of the vulcanization plateau (see Table 9). These tests are completed by the data in Tables 12 and 13, which give the results of tests of the threshold of reaction at 145° C and synesis at room temperature.

PROSTHESIS-SYNESIS WITH FORMALDEHYDE WITHOUT RESORCINOL

PROCEDURE

This reaction was carried out in the presence of hydrogen chloride, which was added to the rubber in the form of rubber hydrochloride. The formaldehyde was added in the form of trioxymethylene.

DIFFERENT FACTORS IN THE REACTION

The effects of increasing proportions of formaldehyde and of hydrogen chloride, and also the effects of heat, were studied so that they could be compared with the action of formaldehyde on prosthetic mixtures.

TABLE 8

All mixtures were heated for 1 hour at 143° C

Mixture	Formaldehyde (parts per 100 parts of rubber)	Swelling in benzene (percentage by volume)	Swelling in gasoline (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
MP ₁	0	307	220	724	211
MP ₁	2	594	456	216	238
MP ₁	5	369	318	171	135
MP ₁	6	335	263	126	106
MP ₁	7	294	228	201	126
MP ₁	8	238	205	350	152
MP ₁	9	211	169	429	127
MP ₁	10	169	142	560	127
MP ₁	20	118	71	702	63
MP ₂	0	262	164	1322	120
MP ₂	2	377	242	353	115
MP ₂	5	204	149	250	50
MP ₂	6	177	148	324	50
MP ₂	7	169	140	434	55
MP ₂	8	135	103	653	55
MP ₂	9	120	100	671	55
MP ₂	10	108	81	918	70
MP ₂	20	81	38	1200	25
MP ₂ extracted	0	346	250	62	87
MP ₂ extracted	2	183	148	762	107
MP ₂ extracted	4	160	134	944	95
MP ₂ extracted	6	132	113	1047	72
MP ₂ extracted	10	123	79	1090	67
MP ₂ extracted	20	85	29	1603	25

TABLE 9

Synthesis			Properties		
Formaldehyde (parts per 100 parts of rubber)	Time of heating (min.)	Temperature (° C)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
10	30	80°	125	920	60
10	30	190°	125	1000	70
10	3	190°	125	1100	60
10	30	145°	135	1050	70
10	60	145°	120	1020	70
10	240	145°	130	950	60

Influence of increasing proportions of formaldehyde.—These tests were carried out with mixtures containing 100 parts of rubber, 5 parts of hydrogen chloride, and various parts of formaldehyde (see Table 10). Each mixture was heated for 1 hour at 143° C.

TABLE 10

Formaldehyde (parts per 100 parts of rubber)	Swelling in benzene (percentage by volume)	Swelling in gasoline (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
1	dissolved	dissolved	—	—
2	1338	908	90	600
4	616	404	215	580
6	502	318	181	345
8	414	252	217	300
10	395	233	215	203
20	273	115	355	121

Influence of increasing proportions of hydrogen chloride.—These tests were carried out with mixtures containing 100 parts of rubber, 10 parts of trioxymethylene, and various parts of hydrogen chloride (see Table 11). Each mixture was heated for 1 hour at 143° C.

TABLE 11

Hydrogen chloride (parts per 100 parts of rubber)	Swelling in benzene (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
0	dissolved	—	—
1.5	356	195	150
3	368	240	150
5	387	210	150
10	429	350	100

It is noteworthy that the proportion of hydrogen chloride seems to be without any great significance, a phenomenon which is far different from that observed in the interaction of rubber, resorcinol and hydrogen chloride.

COMPARATIVE STUDY OF THE ACTION OF FORMALDEHYDE ON
RUBBER IN THE PRESENCE OF HYDROGEN CHLORIDE
AND THE ACTION OF FORMALDEHYDE ON
PROSTHETIC MIXTURES

The influence of the time of heating at 143° C on the following three mixtures were studied:

S	Rubber	100
	Hydrogen chloride	5
	Trioxymethylene	10
S ₁	Prosthetic mixture MP ₁	
	Trioxymethylene	10 parts per 100 parts of rubber
S ₂	Prosthetic mixture MP ₂	
	Trioxymethylene	10 parts per 100 parts of rubber

MP₁ and MP₂ are the prosthetic mixtures which have been described earlier and the data on which are summarized in Table 8. Tests of Mixtures S, S₁ and S₂ are given in Table 12. In all cases the mixtures were heated at 143° C.

TABLE 12

Mixture	Time of heating (minutes)	Swelling in benzene (percentage by volume)	Swelling in gasoline (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
S	3	dissolved	dissolved	—	—
S	15	450	323	88	60
S	60	380	227	185	215
S	180	470	254	177	225
S ₁	3	222	193	417	140
S ₁	15	194	168	500	111
S ₁	60	186	147	514	108
S ₁	180	176	143	480	100
S ₂	3	163	130	570	78
S ₂	15	138	117	657	64
S ₂	60	127	91	722	58
S ₂	180	122	104	742	57

The data in Table 12 show that the affinity of formaldehyde for prosthetic mixtures is greater than for rubber which has only been hydrochlorinated. This is confirmed by the fact that even at room temperature formaldehyde reacts with prosthetic mixtures²³, whereas it does not seem to have any effect on rubber hydrochloride. This is evident from the data in Table 13, which show the swelling of the various samples after having rested for different lengths of time after mixing. These tests were carried out with the same mixtures as those the data on which are recorded in Table 12.

TABLE 13

Mixture	Time of rest after mixing at room temperature	Swelling in benzene (percentage by volume)	Swelling in gasoline (percentage by volume)	Tensile strength (g. per sq. mm.)	Elongation at rupture (percentage)
S (crude)	30 days	dissolved	dissolved	—	—
MP ₁ (control)	not mixed	620	380	—	—
S ₁ (MP ₁ +10% HCHO)	5 hours	740	566	—	—
S ₁ (MP ₁ +10% HCHO)	20 days	283	228	—	—
MP ₂ (control)	not mixed	435	290	—	—
S ₂ (MP ₂ +10% HCHO)	5 hours	351	262	200	119
S ₂ (MP ₂ +10% HCHO)	1 day	—	—	310	70
S ₂ (MP ₂ +10% HCHO)	2 days	—	—	415	70
S ₂ (MP ₂ +10% HCHO)	6 days	—	—	478	70
S ₂ (MP ₂ +10% HCHO)	20 days	154	116	—	—

REFERENCES

- 1 Le Bras, Centre de Perfectionnement Technique, Conference No. 504 (1940).
- 2 Van Rossem, *India-Rubber J.* **92**, 845 (1936).
- 3 Koenigs, *Ber.* **23**, 3144 (1890); **24**, 179 (1891); Koenigs and Carl, *Ber.* **24**, 3889 (1891).
- 4 Since the discovery of vulcanizing agents which are effective without sulfur, the term *vulcanization* no longer signifies treatment with a specific reagent, but a fundamental change brought about by a whole group of reagents and by reactions the limitations of which are as yet not known. It is necessary, therefore to decide upon the essential character of this change before being in a position to say whether or not a material is vulcanized. Rubber vulcanized by sulfur differs from crude rubber chiefly in two characteristics: (1) It has been converted from a predominantly plastic state to a predominantly elastic state; (2) It has thereby become insoluble in solvents. The first of these conditions is essential, and is in itself sufficient indication that vulcanization has taken place. This change from the plastic to the elastic state has, in all reactions known up to the present time, been accompanied by a loss of solubility in solvents, so that this change to the insoluble state may also be regarded as an essential one, although not in itself a sufficient criterion of vulcanization. Since an increase in tensile strength is not always brought about by vulcanization, such a change is not a necessary condition of vulcanization, and is still less sufficient in itself to indicate vulcanization.
- 5 Fisher, U. S. patent 1,642,018 (1927); 1,852,294 (1932); 1,852,345 (1932).
- 6 On this subject, see also Staudinger and Widmer, *Helv. Chim. Acta* **7**, 844 (1924).
- 7 Weber, "The Chemistry of India Rubber", Griffin, London, 1919, p. 33; *Ber.* **33**, 791 (1900).
- 8 Fisher, Gray and McCollm, *J. Am. Chem. Soc.* **48**, 1309 (1926).
- 9 Geiger, *Helv. Chim. Acta* **10**, 530 (1927).
- 10 Low, Rec. communications Congr. Intern. Caoutchouc, 1937, p. 203.
- 11 Rubber-Stichting, French patent 861,306 (1941).
- 12 Greth, *Kunststoffe* **28**, 129 (1938).
- 13 Kirchhof, *Chem.-Ztg.* **47**, 513 (1923).
- 14 I. G. Farbenindustrie A.-G., British patent 486,878 (1937).
- 15 By way of comparison, some experiments were carried out in which the rubber hydrochloride was replaced by commercial chlorinated rubber. The results were negative.
- 16 Bruni, *Rev. gén. caoutchouc* **8**, No. 75, 19 (1931).
- 17 Fisher, U. S. patent 1,852,295 (1932).
- 18 Hesse, *Ann.* **289**, 61 (1895).
- 19 Koenigs and Mai, *Ber.* **25**, 2649 (1892).
- 20 In some of the experiments, these polymers of formaldehyde were replaced by derivatives of formaldehyde, e.g., methylacetal, CH₃(OCH₂)₂, and chloromethyl oxide, CH₂COCH₃, and by formaldehyde in vapor form. The results were quite similar to those obtained with trioxymethylene and with paraformaldehyde.
- 21 This does not exclude the possibility of a vulcanization by resins of the phenol-formaldehyde type (see Reference 11), but under different operating conditions. It is evident that the general mechanism of prothesis-synthesis is applicable to the phenolic nuclei of such resins, just as it is to resorcinol.
- 22 E. I. du Pont de Nemours & Co., British patent 423,520 (1935); *C.A.* **29**, 4374 (1935).
- 23 Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
- 24 Dufraisse and Velluz, Communication presented at the Franco-British Rubber Congress, Paris, May 1940.
- 25 Oenslager, U. S. patent, 1,841,295 (1932).
- 26 Pence, *J. Ind. Eng. Chem.* **3**, 820 (1911).
- 27 Dufraisse and Houpillart, *Rev. gén. caoutchouc* **16**, 44 (1939).
- 28 See earlier section on the "Mechanism of the Mixed Reaction with Resorcinol and Formaldehyde".

THE MAGNETIC ANISOTROPY OF RUBBER *

(MRS.) EUGENIE COTTON-FEYTTIS

In experiments on the magnetic properties of some crystals, one of these crystals was suspended between the poles of a small electromagnet. These poles were flat and of the same diameter as the cores (5 cm.), while the air gap varied from 1.5 to 4 cm. and the field at the center from 8800 to 5500 gauss units.

The crystal was suspended by a silk thread with very slight twist and a small rubber ring cut from a piece of gas tubing. It was observed that, as soon as the electric field was set up, the assembly oriented itself strongly, and the couple exceeded the magnitude which was expected. It was observed also that this couple continued when the crystal was removed and only the rubber ring remained as a possible cause of the phenomenon.

The same phenomenon is observed with a ring of paramagnet rubber and with a ring of diamagnetic rubber, whether the rubber is supple or whether it has become brittle, and whether the ring is perfect or whether it has a cut in it. Instead of flat rings, longer sections of tubing, *e.g.*, 2 to 3c m. long, can be suspended in the magnetic field. It is then particularly surprising to observe that the pieces of tubing always orient themselves axially in the magnetic field, whereas under the same conditions elongated isotropic substances orient themselves in this way only if they are paramagnetic.

In the experiments just described, commercial samples of rubber were used. Samples of this kind are vulcanized, usually contain added ingredients, and during their manufacture have undergone various kinds of mechanical treatment. In view of this, the experiments were repeated with rubber obtained directly by simple coagulation of latex¹. By putting latex in a test-tube (25 mm. long and 6 mm. in diameter) and adding a drop of acetic acid, small strips were easily obtained, and these were suspended at their middle points in the air gap.

It was found that the coagulum, which was diamagnetic like the latex, oriented itself diametrically in the magnetic field in the same way that a strip of a diamagnetic isotropic substance does under the same conditions. But this was no longer true after the cylinder was under a sufficiently high stress for it to be permanently deformed. For example, in one experiment a cylinder was attached by its two ends to two bone rings and stressed by a force of 1 kilogram for 36 hours at 6° C. Its length, originally 2 cm., increased to 7.8 cm. A piece of this stretched cylindrical test-specimen, when examined as before, was found to be oriented to 60° of the lines of force. Another small cylindrical test-specimen of coagulated latex was racked, *i.e.*, it was stretched while immersed in hot water, and was immediately plunged into cold water. These two operations were repeated several times. The elongated cylindrical test-specimen obtained in this way was immediately suspended in the magnetic field, parallel to the lines of force.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 3, page 91, March 1942. This paper was also published in the *Comptes Rendus des Séances de l'Académie des Sciences*, Vol. 214, pages 485-488 (1942). Another paper in continuation of the same subject was published in the *Comptes Rendus*, Vol. 215, pages 299-301 (Oct. 12, 1942), and has already been published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 18, pages 8-9 (January 1945).

Larger cylindrical test-specimens (*e.g.*, 1.5 cm. diameter), prepared from coagulated latex, were compressed, either by flattening them out directly in a press, or by enclosing them in a wooden mould so that they kept their cylindrical form. By suspending them in a horizontal magnetic field in such a way that the direction in which the compression was exerted was itself horizontal, it was found that, as soon as the magnetic field was set up, they took a position perpendicular to the lines of force.

These experiments with coagulated latex explain similar experiments which were made with samples of commercial rubber products which had been subjected to mechanical working, either during their manufacture or subsequently. Whatever the composition of a sample and whether or not it was paramagnetic or diamagnetic, it was found that the direction in which it was held stretched always tended to orient itself parallel to the lines of force, while the direction in which it was compressed oriented itself at right angles to these lines of force. It was found also that the magnitude of the orienting couples increased with the extent of the deformation. Thus when a rubber band was wound for various numbers of turns on the diameter of a cork disc and the system was suspended horizontally in a magnetic field, it was observed that the time of oscillation of the system, whose moment of inertia remained virtually constant, diminished as the number of turns of the rubber band increased.

These facts merit comparison with the almost forgotten experiments which Tyndall carried out nearly one hundred years ago² on the changes in the magnetic properties of various substances brought about by compression. For example, in the case of wax, which is diamagnetic, and in the case of a cube obtained by compressing powdered bismuth, which likewise is diamagnetic, Tyndall found that the same law held true as that stated above for the orientation in a magnetic field. With a paramagnetic substance, *e.g.*, siderite, in powdered form, the direction of compression orients itself in the direction of the lines of force.

If, in the present case, the orientation is the same whether the rubber is paramagnetic or diamagnetic, this is without doubt because the substance which possesses elastic properties is diamagnetic, and it is the superadded load which in some cases makes the assembly attracted to a magnetic pole.

An explanation of this magnetic anisotropy is doubtless to be found in the heterogeneous distribution of the components of the stretched or compressed substance. It is possible to explain some of the already familiar phenomena shown by rubber, *e.g.*, the double refraction of a stretched sheet of rubber, and the diagrams obtained by x-rays or by electronic diffraction.

The present author has found that synthetic rubber shows the same magnetic anisotropy as does natural rubber. Other plastic materials which are quite different from rubber, *e.g.*, Plexiglas, were also found to be magnetically anisotropic. Since this property is easy to identify and to measure, it might be useful in deciding whether two articles which appeared to be the same were actually made in the same way or had been subjected to the same mechanical working.

REFERENCES

- ¹ The author wishes to express her gratitude to the French Rubber Institute for its furnishing her with samples of latex and of rubber.
- ² Tyndall, "Researches on Diamagnetism and Magneto-crystalline Action," Longmans, Green & Co., London, 1870.

THE STRUCTURE OF POLYISOPRENES

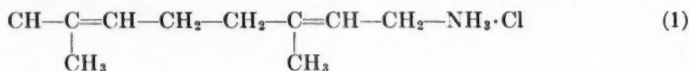
I. THE CRYSTAL STRUCTURE OF GERANYLAMINE HYDROCHLORIDE *

G. A. JEFFREY

INTRODUCTION

The difficulty of crystal structure determination of complex organic molecules is to some degree offset by the extent of the diffraction data. With polyisoprenes much of this information is obscured both by the diffuse nature of the fiber diagrams and by ambiguities arising from imperfect crystallite orientation. The resulting lack of precision is well illustrated by the example of rubber, where attempts at direct analysis have led to considerable disagreement even in the preliminary description of the unit cell¹. The detailed structures of rubber and β -gutta-percha recently proposed by Bunn² are subject to the same limitations, and cannot be regarded as necessarily final solutions, particularly as they entail surprisingly large valency distortions of a type hitherto unparalleled.

With the object of determining indirectly the interatomic dimensions in these polymers, attention has been directed to simpler analogs. Following the study of a monoisoprene compound by Cox and Jeffrey³, derivatives of geraniol were considered, since they possess a diisoprene system akin to the repeating units in the long-chain polymers. Although many of these compounds are unsuitable for x-ray methods, the hydrochloride of geranylamine (1) afforded the requisite crystals for intensity measurements, and their favorable space group, together with the presence of a comparatively heavy chlorine atom, has made possible the complete and accurate analysis of the structure:



EXPERIMENTAL

Four molecules of $\text{C}_{10}\text{H}_{18}\text{NH}_2 \cdot \text{HCl}$ are associated by the space-group symmetry P_{21}/c in a unit cell of dimensions: $a = 22.68 \text{ \AA}$, $b = 5.94 \text{ \AA}$, $c = 8.98 \text{ \AA}$, $\beta = 98.8^\circ$. A complete description of the structure, excluding the hydrogen atoms, therefore requires the determination of 36 atomic parameters. For this purpose, all plane reflections within the range of $\text{Cu } K_\alpha$ radiation were recorded on oscillation photographs about the principal axes, and their relative intensities were estimated by eye with the aid of calibration charts. As it is important that these values should be absolute, they were related to selected intensities transmitted through a thin crystal slab and measured by photometric comparison with a standard rock-salt (400) reflexion recorded on the same film.

* This paper represents Publication No. 61 of The British Rubber Producers' Research Association. It was also published in the *Proceedings of the Royal Society*, Vol. 183, Part A, pages 388-404 (1945). Six pages of tabulated data on calculated and observed structure factors are omitted from the present reprinted version.

All photographs were taken three or more times with different exposures, using aluminum screens of known absorption to bring strong spots within the range of linear x-ray density.

From the experimental measurements the structure amplitudes of 1060 planes were calculated by the usual formulas, and were used first in the summation of a three-dimensional F^2 (Patterson) Fourier synthesis.

THE ARRANGEMENT OF THE CHLORINE ATOMS

The positions of the chlorine atoms were derived directly from the Patterson synthesis by virtue of the outstanding Cl-Cl vector peaks, two at coordinates (0.107, 0.50, 0.162) and (0.107, 0.50, 0.662) and a third of double height at (0.00, 0.00, 0.50). These peaks must arise from atoms at either (0.053, 0.25, 0.081) or (0.053, 0.25, 0.331) in conjunction with atoms symmetrically related. The former was ultimately shown to be correct, but both possibilities had to be considered, since no distinction can be made between the center of symmetry and the screw axis for atoms on the glide planes.

The Patterson synthesis, having symmetry planes at $y = 0$ and $\frac{1}{2}$, cannot reveal any small departure in the y parameter from 0.250. This was assumed to be exact for the approximate structure, and during the successive refinements no evidence to the contrary was observed. Further confirmation was available at the conclusion of the analysis from the comparison of the agreement between observed and calculated structure amplitudes for planes with l odd, where the chlorines make zero contribution, and those with l even:

$$\frac{\sum |F_{\text{obs.}}| - |F_{\text{calc.}}|}{\sum |F_{\text{obs.}}|} \quad 17.0 \text{ and } 17.8\% \text{ respectively}$$

As shown in Figures 4 and 5, these halogen atoms lie in sheets close to the (100) planes enclosing the organic molecules in pairs between them.

DETERMINATION OF THE APPROXIMATE STRUCTURE

The general orientation of the molecules was apparent from the length of the a axis; and from the weak odd layer lines on the c axis photographs it was clear that other atoms besides, the halogens must lie on or near the glide planes. Further information was derived from the Patterson synthesis, which was computed over sections parallel to (010) at intervals of y sufficiently close to reveal all prominent peaks. Six such peaks of height corresponding to Cl-N and Cl-C distances indicated positions for N, C₁, and C₂ in which the nitrogen was equidistant from four chlorine atoms and the interatomic distances and valency angles were approximately normal. This was the only arrangement compatible with the vector maps. Beyond this stage, however, these became much more complicated, and further direct interpretation was not possible. For the remaining eight atoms trial-and-error methods were adopted, and the Patterson synthesis was useful only in restricting the number of possibilities to be considered.

A model based on normal interatomic dimensions was used, first to ascertain arrangements which would satisfy the principal structure factors of the ($h0l$) zone, and then for further trials with general planes. Owing to the wide range of free rotation about each single bond, a large number of configurations was tried and rejected before arriving at a set of coordinates which, when refined by Fourier F synthesis, resulted in a marked improvement in the agree-

ment between the observed and calculated structure factors. These and all subsequent syntheses were of the three-dimensional type, since projections were of little value even on the most favorable (010) plane.

THE FOURIER F SYNTHESIS

Starting from the approximate structure, the atomic coordinates were refined by the method of successive Fourier syntheses. The summations were evaluated from all the available data using Beevers and Lipson's strips⁴ over sections and along lines at values of x , y and z appropriate to the maximum of each atom peak. After the fifth series, the structure-factor calculations re-

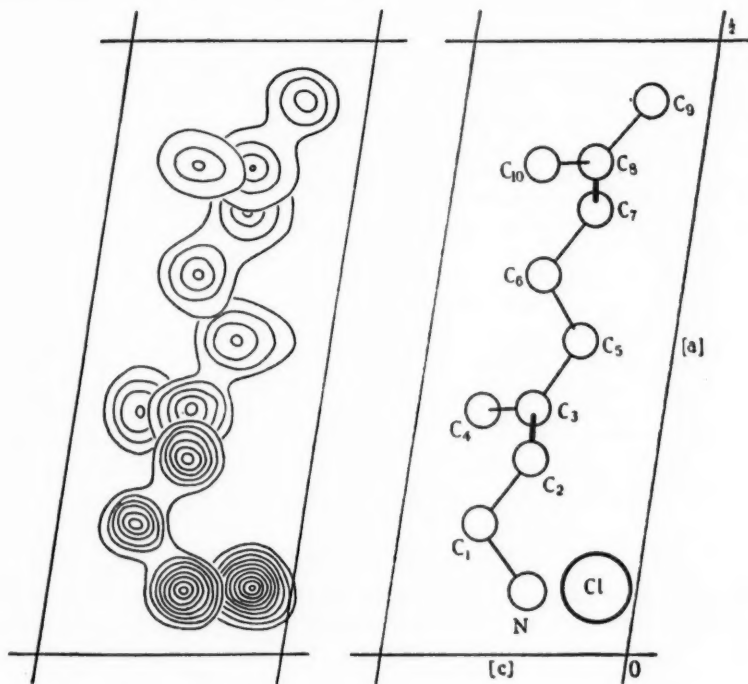


Fig. 1.—Projection of the molecule and Fourier sections on (010).

vealed no further sign changes, and the electron maps from this final summation are shown in Figures 1 and 2. For the purpose of illustration, the electron density peaks for one molecule have been taken from the sectional summations and superimposed on the b and c planes, respectively. The contours are at intervals of one electron per \AA^3 , with the exception of the chlorine atom where the scale is two electrons. The zero and first contours have been omitted for clarity in the diagrams. These maps show clearly that the peaks are different for carbon atoms at opposite ends of the molecule, and although approximately equal in total volume, they become progressively flatter for each atom along the chain from the nitrogen. While it cannot be certain that this has a real physical significance and does not arise merely from the use of a finite Fourier

series, the magnitude of the effect suggests that it may be attributed to a variation in thermal motion between the polar and nonpolar ends of the molecule.

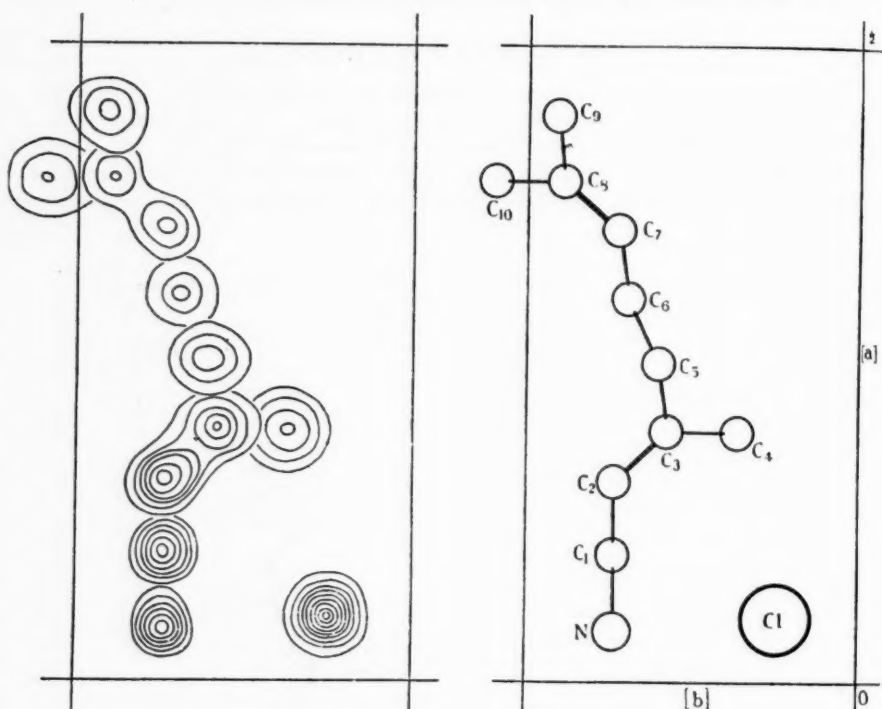


FIG. 2.—Projection of the molecule and Fourier sections on (001).

THE FINAL ATOMIC PARAMETERS

The atomic parameters were measured directly from the maximum of each peak in the Fourier synthesis and gave the interatomic dimensions shown in Table 1.

TABLE I

N-C ₁	1.49 Å	(1.48)	C ₅ -C ₆	1.44 Å	(1.45)
C ₁ -C ₂	1.54	(1.53)	C ₆ -C ₇	1.51	(1.52)
C ₂ -C ₃	1.31	(1.32)	C ₇ -C ₈	1.31	(1.32)
C ₃ -C ₄	1.53	(1.53)	C ₈ -C ₉	1.53	(1.55)
C ₃ -C ₅	1.51	(1.54)	C ₈ -C ₁₀	1.54	(1.53)
N-C ₁ -C ₂	109°	(109°)	C ₃ -C ₅ -C ₆	115°	(112°)
C ₁ -C ₂ -C ₃	126°	(126°)	C ₅ -C ₆ -C ₇	112°	(112°)
C ₂ -C ₃ -C ₄	124°	(124°)	C ₆ -C ₇ -C ₈	129°	(129°)
C ₂ -C ₃ -C ₅	121°	(119°)	C ₇ -C ₈ -C ₉	124°	(123°)
C ₄ -C ₃ -C ₅	115°	(117°)	C ₇ -C ₈ -C ₁₀	121°	(121°)
			C ₈ -C ₉ -C ₁₀	115°	(116°)

The general correctness of this solution is substantiated by the satisfactory agreement between the observed and calculated structure factors for all planes,

and in place of the complete numerical list of 1060 values, which was submitted with the paper but not published, this agreement is shown diagrammatically in Figure 3 for some 500 values.

To examine the accuracy of the results two further Fourier syntheses were evaluated. The full experimental data used previously contained a greater number of observed intensities for the l even series of planes than for the l odd by reason of the comparatively heavy chlorine atom contributing to the former but not the latter. It seemed advisable when locating the carbon atoms that the summations from the l even and l odd planes should include an equivalent number of terms. The synthesis was therefore repeated for the carbon skeleton, omitting those F values (c. 350) where the difference between F_{observed} and F_{chlorine} was less than 1.5 per molecule, this value being the minimum observable when F_{chlorine} was zero. The new atomic positions showed a mean shift of 0.02 Å from those previously derived. The corresponding interatomic distances are given in parenthesis in Table 1.

As an alternative method of balancing the l even and l odd terms, the F values were calculated for all planes of spacing greater than 0.9 Å whose intensities were too small to be observed. These amounted to some 300 values, which when included in the synthesis, also resulted in shifts in the parameters of the order of 0.02 Å and, as might be expected, considerably sharpened the electron peaks. The double bond lengths became 1.34 Å, the C₅-C₆ bond 1.46 Å, and the other bonds remained the same within 0.01 Å. The progressive broadening of the countour intervals for each atom along the molecule was still clearly apparent, although the additional terms increased the maximum electron density of the peaks other than those at $y = \frac{1}{4}$ and $\frac{3}{4}$ by about $\frac{1}{2}$ electron/Å³.

Both these Fourier syntheses were an improvement on the original as regards the shape of the electron contours, particularly those of C₅ where the elongation of the peak in the c axis direction was completely removed. The changes in peak positions were of the same order as those between the penultimate and final successive Fourier syntheses, and the bond lengths and valency angles showed no variations beyond the limits of experimental errors which are estimated at ± 0.04 Å and $\pm 4^\circ$.

Although the atom peaks were least sharp in the synthesis using the smaller number of F values, these atomic parameters (Table 2) are considered to be the most reliable, since they were derived solely from experimental data with the exclusion, for the organic part of the molecule, of such values as might impose a systematic error on the positions of the maxima.

TABLE 2

	x	y	z		x	y	z
Cl	0.053	0.250	0.080	C ₅	0.253	0.625	0.182
N	0.049	0.750	0.216	C ₆	0.304	0.700	0.287
C ₁	0.103	0.750	0.333	C ₇	0.357	0.746	0.207
C ₂	0.158	0.751	0.255	C ₈	0.394	0.916	0.212
C ₃	0.198	0.593	0.264	C ₉	0.447	0.918	0.118
C ₄	0.198	0.379	0.358	C ₁₀	0.392	1.120	0.315

THE STEREOCHEMISTRY OF THE MOLECULE

Within experimental error the two isoprene units are identical, the parameters of C₁-C₅ being more certain than C₆-C₁₀, owing to the flattening of the Fourier peaks described above. They possess normal bond lengths (C=C 1.34 Å, C—C 1.54 Å) and the disposition of valencies about the double bonds

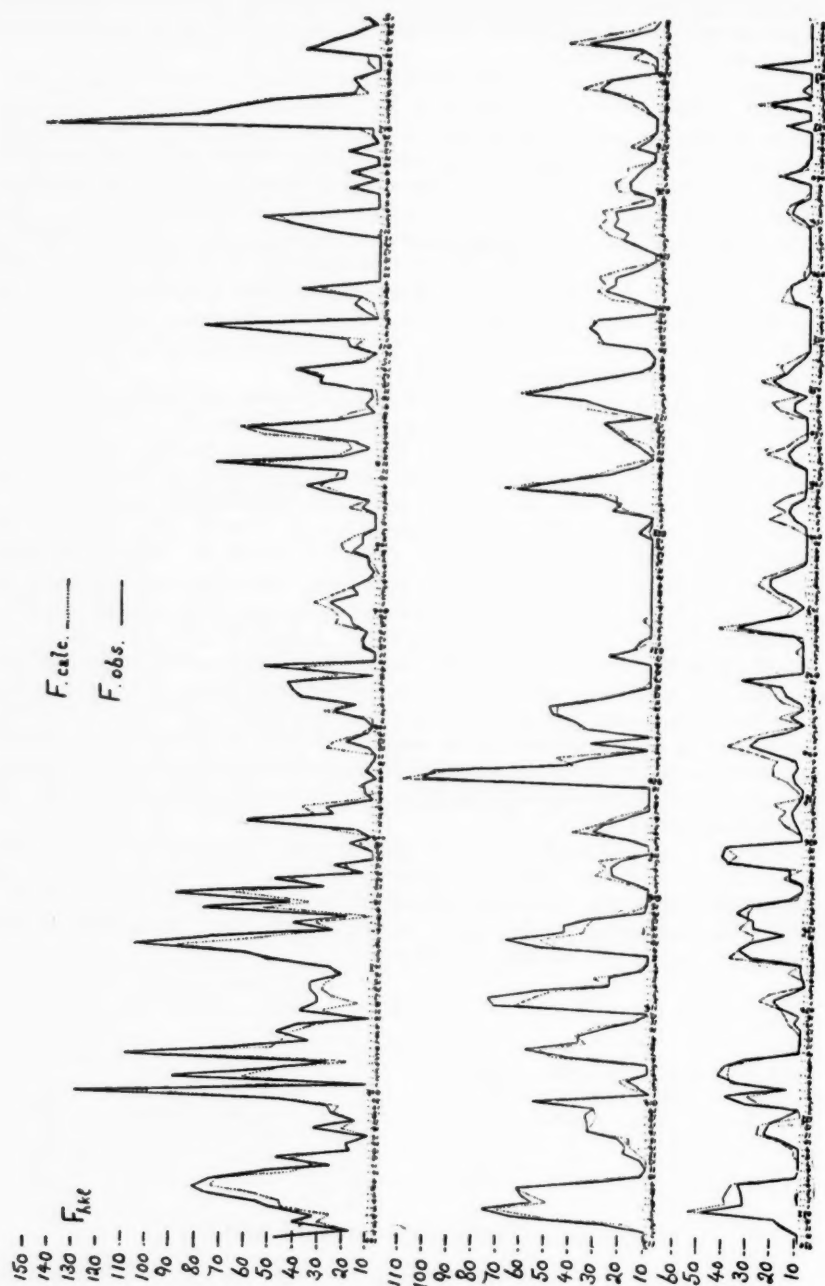


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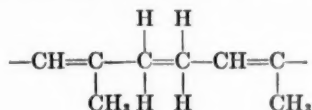
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is planar. Their angles appear to be distorted by about 5° from the theoretical 120° , with the result that C_1-C_2 is not exactly parallel to C_3-C_5 nor C_6-C_7 to C_8-C_9 . This variation, although small and very near the margin of error, may be real and characteristic of the unsymmetrical arrangement of the groups about the double bond.

The bond C_5-C_6 linking the isoprene units is shorter than that associated with a normal C-C bond by an amount two or three times the probable experimental error. Furthermore the distribution of the adjoining C_3-C_5 and C_6-C_7 is planar. These features, reminiscent of those found in conjugated molecules, seem inexplicable in terms of the usual theory of mesomerism. As reported by Bateman and Jeffrey⁵, the amine hydrochloride group does not appear to be directly responsible, and the hybrid character may result from a hyperconjugation process in which the α -methylenic C-H electrons become partially localized in the central bond:



Evidence as to what extent this can be regarded as a general property of the polyisoprene system must await the examination of compounds with a similar structural modification.

Other stereochemical features of importance in the geranylamine structure concern the angular position of the C_5-C_6 bond relative to the two isoprene planes. Free rotation about the bond C_3-C_5 is influenced by repulsion of the CH_2 group by the CH and CH_3 . If the CH_2 group lies in the plane of the isoprene ($C_1 \cdots C_5$), then the approach between one or other pair of these atoms would be of the order of 2.8 Å; a distance which in the absence of any special bonding between the hydrogen atoms provides an appreciable energy barrier. In the observed structure the C_5-C_6 bond is oriented at 80° to the isoprene plane and the steric repulsions balance at almost equal distances (C_6-C_2 3.28 Å, C_6-C_4 3.24 Å). In contrast, since there is no methyl addendum to C_7 , the rotation about C_6-C_7 relative to the other isoprene plane is influenced solely by the approach of the CH_2 to the CH_3 ($_{10}$). Over a large angular range, this repulsion is ineffectual, and the factors determining the observed angle of 45° between the C_5-C_6 bond and the $C_6 \cdots C_{10}$ plane must arise mainly from the packing of adjacent molecules in the crystal lattice, and probably from the relation between the terminal $\text{C}(\text{CH}_3)_2$ groups in particular. Whereas this latter steric effect is specific to the particular intermolecular arrangement, the former depends on intramolecular forces and, since it applies to any molecule with the same configuration, has an important bearing on the stereochemistry of the long-chain polymers.

THE INTERMOLECULAR ARRANGEMENT

The packing of the molecules in the crystal lattice is illustrated in Figures 4 and 5. The hydrocarbon chains lie parallel with the molecules end to end in pairs. Each nitrogen is associated with four chlorine atoms at nearly equal distances.

All other distances between atoms in adjacent molecules conform to Van der Waal's forces and are greater than 3.75 Å with the exception of 3.60 Å between centrosymmetrically related C_9 atoms.

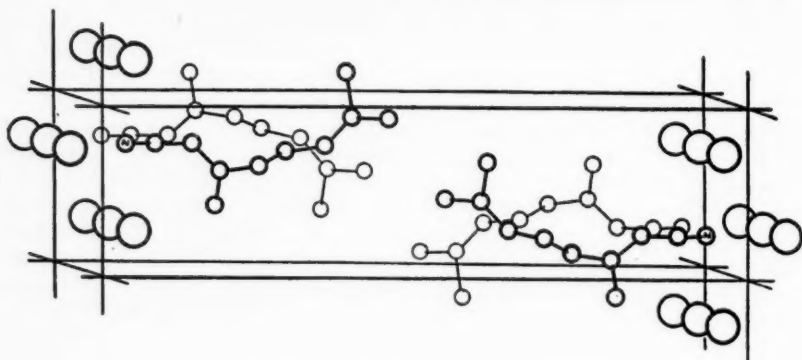


FIG. 4.—The structure of geranylamine hydrochloride.

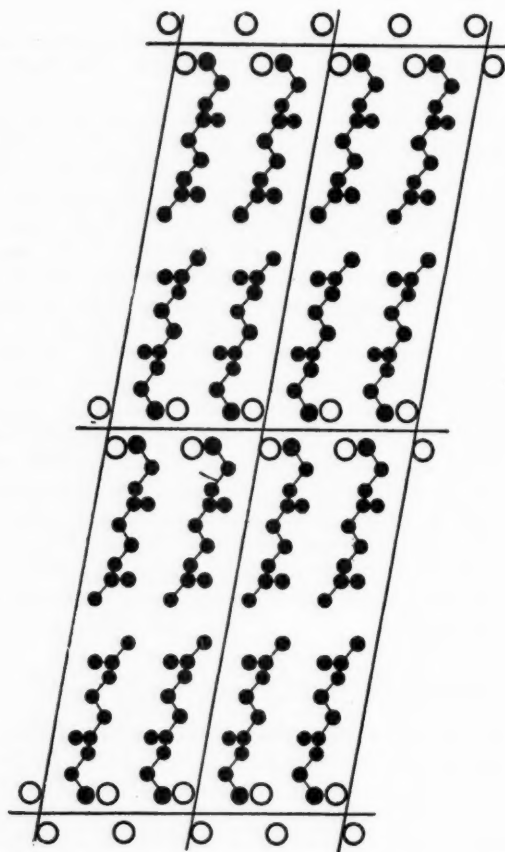


FIG. 5.—Projection of the structure on (010).

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TABLE 3

N-Cl ₁	3.24 Å	N-Cl ₃	3.24 Å
N-Cl ₂	3.17	N-Cl ₄	3.24

SUMMARY

An x-ray analysis employing three-dimensional Fourier syntheses has established the crystal structure and molecular dimensions of the diisoprene derivative, geranylamine hydrochloride. The molecules, which have a trans-configuration and are therefore analogous to gutta-percha, lie parallel and end-to-end in pairs within an ionic framework, where each nitrogen atom is equidistant from four chlorine neighbors. The two isoprene units are planar and have normal interatomic distances, but are linked by a C-C bond markedly shorter than a normal single bond. This unusual bond feature is accompanied by a coplanar arrangement with the adjacent carbon bonds.

ACKNOWLEDGMENTS

I am grateful to Professor Sir Lawrence Bragg and E. G. Cox for advice and criticism and to Professor W. N. Haworth for facilities granted at Birmingham University for the earlier part of the work. Thanks are also given to D. A. Sutton for preparation of the geranylamine hydrochloride.

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REFERENCES

- ¹ Lotmar and Meyer, *Monatsh.* **69**, 115 (1936); Sauter, *Z. physik. Chem.* **36B**, 405 (1937); Moras, *J. Am. Chem. Soc.* **60**, 273 (1938); Misch and van der Wyk, *J. Chem. Physics* **8**, 127 (1940).
- ² Bunn, *Proc. Roy. Soc.* **180A**, 40 (1942).
- ³ Cox and Jeffrey, *Trans. Faraday Soc.* **38**, 241 (1942).
- ⁴ Beevers and Lipson, *Proc. Phys. Soc.* **48**, 772 (1936).
- ⁵ Bateman and Jeffrey, *Nature* **152**, 446 (1943).

THE NATURE OF THE DYNAMIC DOUBLE REFRACTION OF RUBBER SOLUTIONS AND THE SHAPE OF RUBBER MOLECULES *

V. TSVETKOV AND A. PETROVA

INTRODUCTION

In an earlier work¹ we described an experimental apparatus with which double refraction and the angle of extinction in a flowing liquid can be measured through a wide range of velocities. This apparatus was used to study the dynamic optical effects of some synthetic rubbers in solution, and it was found that, by measuring the angle of extinction, it is possible to estimate the diffusion coefficient and the mean linear dimensions of the particles of a dissolved polymer.

In addition to this, evidence was obtained that the particles of synthetic polymers are smaller than those of natural rubber and polystyrene. However, this method did not indicate any essential differences in the diffusion coefficients of the various synthetic rubbers which were examined, and therefore it proved to be little suited for comparing polymers which differ only slightly in molecular weight.

A more sensitive method for studying the shape of particles is to measure their double refraction. However, it is still impossible to do more than draw certain general conclusions as long as the physical nature of the effects observed remain uncertain.

In addition to obtaining further information by a study of a large number of new samples of synthetic rubber, it was attempted in the present work to choose, on the basis of experimental data, between existing theories of the double refraction of a flowing solution and to apply the particular theory chosen to the calculation of the shape of the particles of a high-molecular substance when in solution.

MAGNITUDE OF DOUBLE REFRACTION AND ANGLE OF EXTINCTION AS FUNCTIONS OF THE VELOCITY GRADIENT

In the present work the apparatus described earlier was used, except that, when studying solutions with only slight double refraction, an elliptical compensator was used (0.02 λ).

The dependence of the dynamic double refraction and the angle of extinction on the velocity of flow of solutions of more than thirty samples of synthetic rubbers, a considerable number of which consisted of polymers of butadiene, was investigated.

Not all the graphs of the samples and their solutions are given, and we shall merely point out that the double refraction Δn of a solution of a synthetic

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polymer usually increases linearly with increase in the rate of shear g ; then, as the angle α , represented by the optical axis in the direction of flow (angle of extinction) diminishes, it remains within the limits of $\pi/4$ and 0. The relations: $\Delta n = f(g)$ and $\alpha = f(g)$ are shown in Figure 1, which shows the results obtained for solutions in naphtha of two types of isoprene polymers, i.e., synthetic analogs of natural rubber.

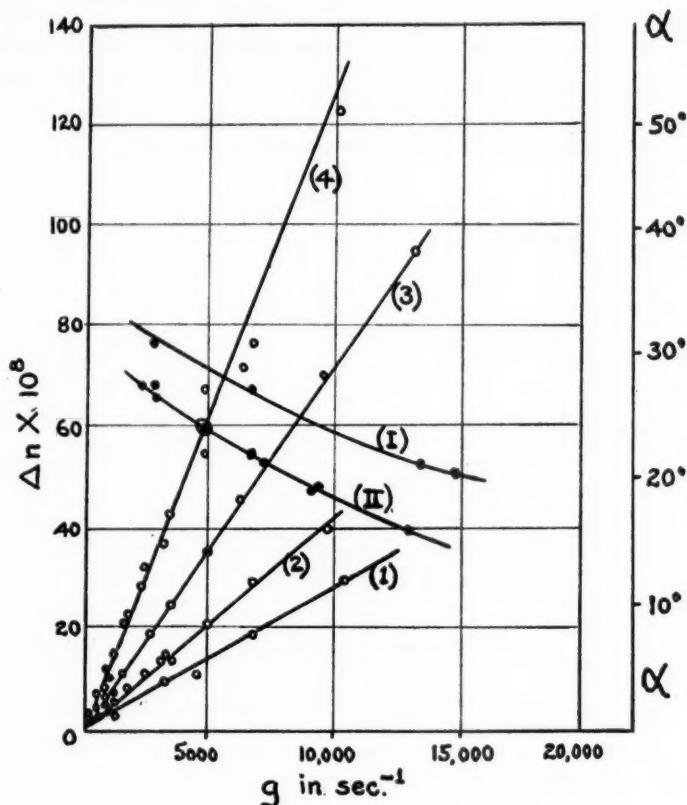


FIG. 1.—Isoprene rubber in naphtha.

$$C_m = 0.33 \begin{cases} 1. \text{ No. 52} \\ 2. \text{ No. 44} \end{cases} \Delta n = f(g)$$

$$C_m = 0.53 \begin{cases} 3. \text{ No. 52} \\ 4. \text{ No. 44} \end{cases}$$

$$C_m = 0.53 \begin{cases} \text{I. No. 52} \\ \text{II. No. 44} \end{cases} \alpha = f(g)$$

Quite similar curves were obtained with a butadiene-styrene polymer (Buna-S), both before and after being plasticized, and also with a whole series of other rubbers.

Usually a polymer with a relatively small molecular weight but with the same g value shows a relatively small double refraction and a relatively large α value. For example, the viscometric molecular weight of isoprene rubber (No. 52) was found to be 26×10^3 , whereas No. 44 rubber showed a value of

35,000. The molecular weight of normal Buna-S in carbon tetrachloride was 44,000; when plasticized, it was 30,000.

A somewhat different $\Delta n = f(g)$ relation was found for polymers having high molecular weights. Here $\Delta n = f(g)$ is represented by a slightly curved line, with its concavity upwards. This applies to solutions of polyisobutylene (Oppanol) ($\mu = 165,000$ in naphtha) and Vistanex ($\mu = 75,000$ in naphtha), as is evident in Figure 2. The relation: $\Delta n = f(g)$ in solutions of natural rubber is of a similar character.

The dynamic optical properties of these polymers are similar to those of high-molecular polystyrenes, for solutions of which Signer² also found a curving of the graph of $\Delta n = f(g)$ with respect to a more rapid increase of Δn .

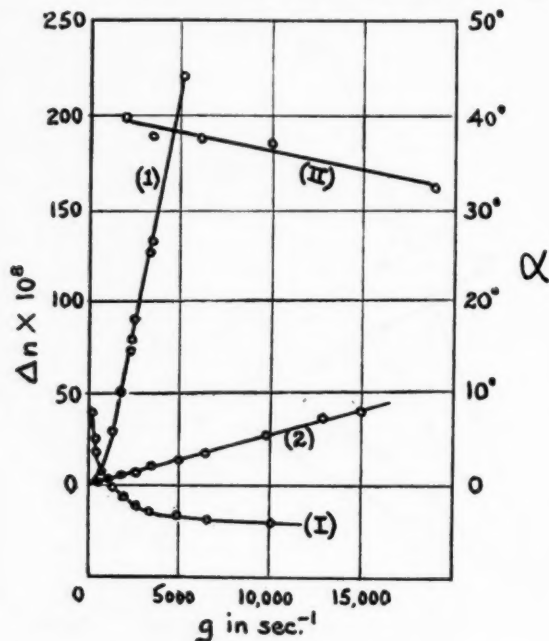


FIG. 2.—Oppanol in naphtha. Curves (1) and (2); $\Delta n = f(g)$; (1) and (II); $\alpha = f(g)$. (I) and (II) unmilled; $C_m = 0.2$; (2) and (II) milled 180 minutes; $C_m = 0.535$.

The angle of extinction in solutions of high-molecular rubbers decreases very sharply as g increases. Thus in the Oppanol solution, $C_m = 0.2$, and the curve $\alpha = f(g)$ intersects the axis g when g reaches a value of 1200 sec.^{-1} , and soon reaches saturation, which lies in the region of negative α (see Figure 2).

The great changes in dynamic optical properties which take place under the influence of milling are characteristic of these polymers, whereas the double refraction values of other synthetic rubbers are but little affected.

As an illustration, let us compare unmilled Oppanol with the same material milled for 180 minutes (see Figure 2). It is evident that milling lowers greatly the $\Delta n = f(g)$ curve and raises greatly the $\alpha = f(g)$ curve.

Since the Δn values of the majority of the synthetic rubbers examined increased proportionally to g , and since in those cases where there was a deviation of the curve from rectilinearity, this deviation was insignificant, we

may characterize the dynamic double refraction of the solution by the relation: $\Delta n/g$.

The values obtained for solutions of various nonbutadiene polymers are given in the sixth column of Table 1, which gives also the corresponding molecular concentrations C_m (in mols of the base molecule per liter of the solution) and the values of the absolute and specific viscosities.

Solutions of samples of technical polybutadiene, purified by the ordinary centrifugal method, often show anomalous dynamic optical properties, which are manifest when the double refraction reaches its maximum value at an insignificant velocity of flow and then decreases very slowly to g values of several thousands sec^{-1} . However, with the greatest increase in rate, the curve $\Delta n = f(g)$ changes direction, then continues to ascend rectilinearly, and does not change its inclination through the entire range of velocities studied (until $g = 50,000 \text{ sec}^{-1}$).

As an example of this, Figure 3 shows a representative curve for the solutions of butadiene rubber (made by the gas process) in naphtha. The measurement of the angle of extinction in these solutions also gives anomalous results which are not easy to reproduce. The $\alpha = f(g)$ curve sometimes has the shape represented in Figure 3; for small g values the angle α increases, reaches its maximum value when g is 10,000–20,000 sec^{-1} , and then decreases slowly. However, in certain cases α varied from values below 45° for small g values to above 45° for large g values. A representative curve was shown in the earlier mentioned work¹.

The curves in Figure 3 indicate that the dynamic optical properties are governed by the presence in the solution of two arrangements of particles; one causing a "normal" effect, the other causing a deviation of the curves from their normal character at small velocities.

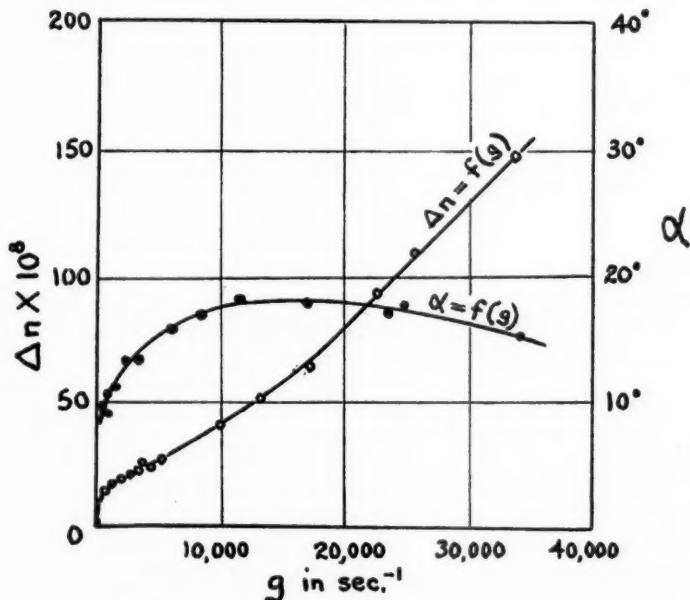


FIG. 3.—Butadiene rubber No. 3893 in naphtha; $C_m = 0.52$.

TABLE 1

Type of Elastomer	Solvent	Molecular Concentration C_m	Specific Viscosity η_{sp}/C	Absolute Viscosity η_{abs}	$\frac{\Delta n}{\rho} \times 10^{10}$	$\frac{\Delta n}{\rho C_m} \times 10^{10}$	$\frac{\Delta n}{\rho C_m \sqrt{\eta_{sp}}} \times 10^{10}$	$\left[\frac{\Delta n}{\rho C_m \sqrt{\eta_{sp}}} \right]_{\infty}$
Smoked Sheets, unmilled	Naphtha	0.13	62.0	0.366	33.5	25.8	56.1	56.1
Smoked Sheets, unmilled	Carbon tetrachloride	0.156	47.0	0.63	50.0	32.0	35.4	35.4
Smoked Sheets, milled	Naphtha	0.160	5.7	0.046	3.5	2.2	12.4	12.4
Isoprene No. 52, milled 1942	Naphtha	0.33	8.4	0.064	2.8	8.4	4.07	3.8
Isoprene No. 52, milled 1942	Naphtha	0.53	24.7	0.176	6.5	12.3	3.55	3.87
Isoprene No. 44, milled 1942	Naphtha	0.33	4.1	0.083	4.1	12.5	5.2	5.57
Isoprene No. 44, milled 1942	Naphtha	0.53	35.0	0.24	12.5	2.36	5.94	5.57
Sovprene, milled	Chloroform	0.50	17.0	0.21	6.75	1.35	2.84	2.84
Vistanex, unmilled	Naphtha	0.54	86.7	0.60	27.5	5.15	8.05	8.57
Vistanex, unmilled	Naphtha	0.33	13.4	0.33	7.5	2.28	7.5	8.57
Vistanex, unmilled	Naphtha	0.27	11.1	0.086	5.0	1.85	7.5	8.57
Vistanex, unmilled	Naphtha	0.20	5.95	0.048	3.6	1.8	9.9	8.57
Vistanex, milled 60 min.	Naphtha	0.134	2.87	0.027	1.9	1.42	9.95	8.57
Vistanex, milled 60 min.	Naphtha	0.33	8.24	0.063	3.0	0.9	4.35	4.1
Vistanex, milled 180 min.	Naphtha	0.535	30.4	0.21	7.76	1.45	3.86	3.32
Vistanex, milled 180 min.	Naphtha	0.33	5.1	0.04	1.72	1.01	3.42	3.32
Oppanol, unmilled	Naphtha	0.535	17.0	0.125	5.4	1.01	34.0	76.2
Oppanol, unmilled	Naphtha	0.20	87.0	0.60	43.3	21.65	69.5	76.2
Oppanol, unmilled	Naphtha	0.134	18.8	0.136	28.25	12.77	18.76	76.2
Oppanol, milled 180 min.	Naphtha	0.068	3.56	0.033	12.77	0.34	125.0	2.38
Oppanol, milled 180 min.	Naphtha	0.535	11.3	0.073	2.86	0.82	2.38	2.38
Buna-S, plasticized	Chloroform	0.68	11.3	0.134	3.4	5.95	2.15	2.15
Buna-S, plasticized	Chloroform	0.68	44.5	0.34	43.3	5.95	2.15	2.15
Buna-S, milled in 1941	Chloroform	0.68	30.5	0.045	13.3	0.75	4.26	3.58
Buna-S, milled in 1941	Naphtha	0.217	6.44	0.056	1.74	0.633	3.38	3.58
Buna-S, milled in 1941	Naphtha	0.275	13.36	0.075	3.53	0.96	3.15	3.15
Buna-S, milled in 1941	Naphtha	0.368	1.24	0.036	1.27	1.25	5.2	4.48
Buna-S, milled in 1941	Tetralin	0.159	3.8	0.036	1.36	0.86	3.94	4.48
Buna-S, milled in 1942	Naphtha	0.22	6.9	0.059	1.82	0.83	4.28	4.48
Buna-S, milled in 1942	Naphtha	0.296	13.5	0.108	3.59	1.22	4.77	4.77
Buna-S, milled in 1942	Tetralin	0.20	1.22	0.039	1.89	1.89	5.77	5.3
Buna-N, unmilled	Naphtha	0.33	1.66	0.0192	5.3	0.698	4.85	5.3
Buna-N, unmilled	Naphtha	0.386	5.4	0.048	3.64	0.92	4.85	5.3
Buna-N, unmilled	Tetralin	0.133	0.8	0.048	1.9	1.04	2.9	2.9
Buna-N, milled	Naphtha	0.232	1.6	0.0195	1.3	0.56	4.63	4.12
Buna-N, milled	Naphtha	0.304	5.3	0.0472	2.27	0.747	3.97	4.12
Buna-N, milled	Naphtha	0.347	6.63	0.0572	2.7	0.778	3.75	4.12
Buna-N, milled	Tetralin	0.366	3.4	0.117	4.57	1.25	2.22	2.22
Budien-styrene polymer milled in 1941	Carbon tetrachloride	0.218	5.00	0.060	1.48	0.68	2.53	2.07
Budien-styrene polymer milled in 1941	Carbon tetrachloride	0.235	5.20	0.068	1.2	0.51	1.88	2.07
Budien-styrene polymer milled in 1941	Carbon tetrachloride	0.273	6.65	0.084	2.17	0.79	2.63	2.07
Budien-styrene polymer milled in 1941	Carbon tetrachloride	0.368	11.70	0.14	2.86	0.78	1.97	2.07
Budien-styrene polymer milled in 1941	Carbon tetrachloride	0.412	14.0	0.165	3.2	0.78	1.82	2.07
Budien-styrene polymer milled in 1941	Benzene	0.250	6.60	0.057	1.1	0.44	2.13	2.13
Budien-styrene polymer milled in 1941	Tetralin	0.358	4.40	0.143	4.73	1.32	2.14	2.14
Butadiene-styrene polymer milled in 1942	Carbon tetrachloride	0.20	4.90	0.065	1.63	0.82	3.1	2.52
Butadiene-styrene polymer milled in 1942	Carbon tetrachloride	0.274	8.60	0.106	2.31	0.85	2.62	2.52
Butadiene-styrene polymer milled in 1942	Carbon tetrachloride	0.332	12.60	0.150	2.9	0.88	2.15	2.52
Butadiene-styrene polymer milled in 1942	Carbon tetrachloride	0.344	11.90	0.142	3.5	1.02	2.57	2.52
Butadiene-styrene polymer milled in 1942	Carbon tetrachloride	0.368	13.70	0.147	4.6	1.02	2.37	2.52
Butadiene-styrene polymer milled in 1942	Benzene	0.374	14.70	0.118	4.72	0.72	2.37	2.52
Butadiene-styrene polymer milled in 1942	Tetralin	0.393	17.50	0.250	7.41	1.65	2.37	2.52

In an effort to substantiate this hypothesis we investigated the optical properties of solutions in a magnetic field and in an electrical field, and found abnormally great double refraction and dichroism. Besides, the curves show that double refraction reached saturation rather quickly. This seems to suggest the presence in the solution of large optical- and magneto-anisotropic particles. Electro- and magneto-optical effects are affected by contamination of the rubber with crystal or colloid particles during milling and refining. There are reasons to believe that they are particles of talc, which is often used in the milling process.

Since centrifugation even for ten hours did not purify the solution sufficiently and did not prevent anomalies in the magnetic and electric fields, recourse was had to electropurification of the solutions. Experimentation showed

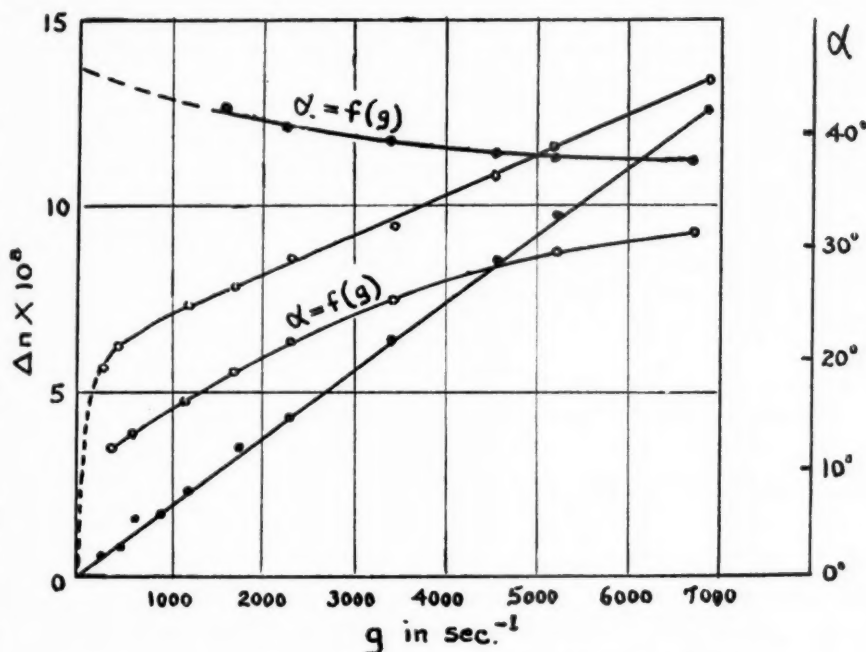


FIG. 4.—Sodium butadiene rubber No. 5418 in naphtha (100–120°). $C_m = 0.49$ Centrifuged 10 hours. ● Purified electrophoretically 3 hours, $E = 6000$ V/CM. ○ Unpurified.

that keeping a solution of butadiene rubber in a strong electric field for several hours led to coagulation of the colloidal mixture and a significant increase in the transparency of the solution. In addition, the abnormally large double refraction in magnetic and electric fields and the anomalous properties during flow, which have been mentioned above, practically disappeared.

This last case is illustrated in Figure 4, which shows the $\Delta n = f(g)$ and $\alpha = f(g)$ curves for a solution of a butadiene polymer before and after purification in an electric field. Before it was placed in the electric field the solution was centrifuged for 10 hours.

It is evident that, for the purified solution, $\Delta n = f(g)$ is a rectilinear function of g , and that with increase in g the angle α normally decreases from an initial value of 45°.

Investigation of the dynamic optical properties of solutions of eighteen samples of butadiene rubber showed that, when sufficiently purified by electrophoresis, solutions give normal dynamic optical effects similar to those of other synthetic rubbers of not too great molecular weights.

The results of these investigations are shown in Table 1.

In cases of contamination by talc, its influence on the calculation of $\Delta n/g$ was manifest by a corresponding displacement of the $\Delta n = f(g)$ curve.

THE DYNAMIC OPTICAL CONSTANT

In comparing results obtained with various polymers, the question of what expression to use in characterizing double refraction is of fundamental importance.

The value $\Delta n/g$ cannot serve this purpose, for it increases with increase in the concentration of rubber in solution and increases faster than the latter. A graphic illustration of this appears in Figure 5, which shows the curve $\Delta n/g = f(C)$ for solutions of Vistanex in naphtha.

Here $\Delta n/(gC)$ increases with increase in C_m (see Column 7, Table 1), apparently because with increase in concentration the viscosity also increases, which leads in turn to an increase in the double refraction effect. According to existing theories of double refraction⁴ of a rubber solution, regardless of its nature, during flow, the value $Z_0 = \Delta n/(gC_m\eta)$ must remain constant.

However, experiments did not substantiate this. The Z_0 value was not only different for different solvents, but did not remain constant for solutions in the same solvent, *i.e.*, it diminished sharply with increase in concentration. The curve $\Delta n/(gC_m\eta) = f(C_m)$ for Vistanex in Figure 5 illustrates this point.

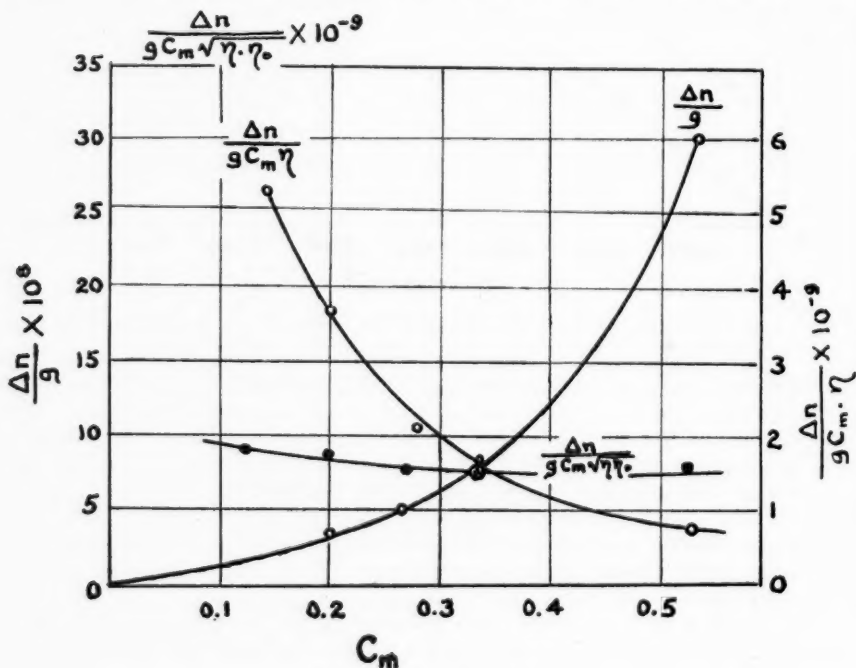


FIG. 5.—Vistanex in naphtha.

Analogous results were obtained for all other rubbers (see Table I). Signer⁵, in his researches on the dynamic optical properties of solutions of polystyrene, arrived at similar conclusions.

The reason for such a discrepancy between theory and experiment seems to lie in an uncertainty in the concept of viscosity, which enters into the expression for Z_0 .

Indeed, in this expression η represents the viscosity coefficient on which the force orientating or extending a particle during flow depends directly.

In the case of dilute solutions, the viscosities of which usually do not differ materially from the viscosity of the solvent, a macroscopic viscosity coefficient is used, which is measured with the aid of a viscometer. Although the validity of such a simplification may be in doubt in a number of cases, very dilute solutions give results which do not contradict experimental data; as for example in the theory of Debye for dielectric losses.

The situation is very different in the case of concentrated solutions of polymers having high viscosities which are influenced to a considerable degree by the interaction of the molecules of the dissolved substance. It is very improbable that in such systems the macroscopic viscosity coefficient would coincide with the microscopic one, which characterizes the force acting on a particle in the liquid.

A graphic example of this is found in systems of anisotropic liquids with strongly interacting particles. Such systems exhibit viscosity anisotropy, as evidenced by the fact that their viscosities depend on the orientation of the molecular axes in relation to the direction of flow⁶. In addition, experiments showed that the effect of temperature on the microscopic viscosity coefficients of these liquids is considerably different from the effect of temperature on their macroscopic viscosities.

Therefore, even in the case of not too dilute solutions of high-molecular substances, it is impossible to identify the macroscopic coefficient of rotary friction η_1 of a particle with the viscosity coefficient of the solution η measured in a viscometer. However, it may be assumed that the first value is independent of the second: $\eta_1 = f(\eta) = f(\eta_0, X)$, when η_0 is the viscosity of the solvent, and X the relative viscosity of the solution. The function f may be determined empirically by studying separately its dependence on X and η_0 .

The experimental data necessary for determining the dependence of η_1 on X with η_0 constant are given in Table 1.

The fact that the $Z_0 = \Delta n / (g C_m \eta)$ value diminishes with increase in concentration shows that, with increase in concentration, the microscopic viscosity coefficient η_1 increases more slowly than the relative viscosity of the solution. The $\Delta n / (g C_m \eta)$ value appears to be approximately independent of the concentration if it is assumed that $\eta_1 \sim \sqrt{x}$. Values of $Z = \Delta n / (g C_m \eta_0 \sqrt{X})$, calculated for all solutions studied, are shown in column 8 of Table 1. The data show that, for all solutions of a given polymer in a given solvent, the Z values are approximately equal. The constancy of the Z value for solutions of Vistanex in naphtha is illustrated by the corresponding curve in Figure 5.

The last column of Table 1 gives values of Z as averages of the values in the preceding column.

Table 2 gives the average values of Z for butadiene rubbers, the molecular weights of polymers determined viscometrically, and their plasticities.

The dependence of η_1 on η_0 when X is constant may be followed by studying the dynamic optical properties of the same solution at different temperatures.

TABLE 2
BUTADIENE RUBBERS

Type of Synthetic Rubber	No.	Plasticity	Molecular weight μ	$\left[\frac{\Delta n}{g C_m \sqrt{\eta \eta_0}} \times 10^3\right]_{\text{ave.}}$
Sodium-butadiene polymer (gas process)	3891	0.26	38,000	3.15
Sodium-butadiene polymer (gas process)	3893	0.26	40,000	3.01
Sodium-butadiene polymer (gas process)	3894	0.28	37,000	2.9
Sodium-butadiene polymer (gas process)	3895	0.25	40,000	3.22
Sodium-butadiene polymer (gas process)	3896	0.24	38,000	3.22
Sodium-butadiene polymer (gas process)	3904	0.25	40,000	3.17
Sodium-butadiene polymer (gas process)	1340	0.24	36,000	3.05
Sodium-butadiene polymer (gas process)	5418	0.41	28,000	2.42
Sodium-butadiene polymer (gas process)	0.610	0.38	29,000	2.26
Freeze-resistant	8123/94	0.48	25,000	2.93
Freeze-resistant	0.641	0.39	28,000	2.96
Freeze-resistant	6	0.36	30,000	3.64
Freeze-resistant	8123/107	—	23,000	3.0
Rod-process	2608	0.46	27,000	2.03
Rod-process	34333	0.49	20,000	2.15
Latex	33890	0.45	18,000	3.37
Latex	76	—	14,000	2.7
Latex	27476	—	11,000	1.96

Experiments showed that warming of a rubber solution through a wide range of temperatures changes its absolute viscosity, whereas its relative viscosity remains constant.

In addition to studying the effect of the temperature on viscosity, we carried out investigations on the dynamic optical properties of the same solution at various temperatures. In this case an apparatus with an electric heater was employed.

The results obtained with Vistanex in tetralin are shown in Figure 6, which gives the curves $\Delta n = f(g)$ and $\alpha = f(g)$ for five temperatures. It is evident that an increase of temperature diminishes the double refraction and increases the curve $\alpha = f(g)$, corresponding to a decrease in the viscosity of the solution.

The Z value was calculated for each temperature, taking into account the change of C_m with increase in t resulting from a decrease in density. The results are given in column 2 of the following table:

DEPENDENCE OF THE DYNAMIC DOUBLE REFRACTION OF A
VISTANEX SOLUTION ON THE TEMPERATURE

Temperature (t °C)	$Z \times 10^3$	Correction for irreversible variation (percentage)	Corrected value of Z
12.5	5.82	0	5.82×10^{-9}
31.4	5.36	7	5.75×10^{-9}
48.5	4.82	14	5.50×10^{-9}
68.2	3.88	20	4.66×10^{-9}
88	2.62	27	3.32×10^{-9}

As is evident from the table, the value of Z decreases with increase in temperature, slowly at first, then relatively rapidly.

The experiments showed irreversible changes in the solution on warming, with a decrease in double refraction. As an illustration of this, see curve 6 in Figure 6, which represents a solution at its original temperature, but after having been warmed for several hours. Comparison with curve 1 shows a decrease of 27 per cent in the effect. Assuming that the percentage diminution $\Delta n/g$ caused by irreversible changes is proportional to the rise in temperature, suitable corrections (column 3) were made for the value of Z , so that the final value, given in column 4 of the table, was obtained.

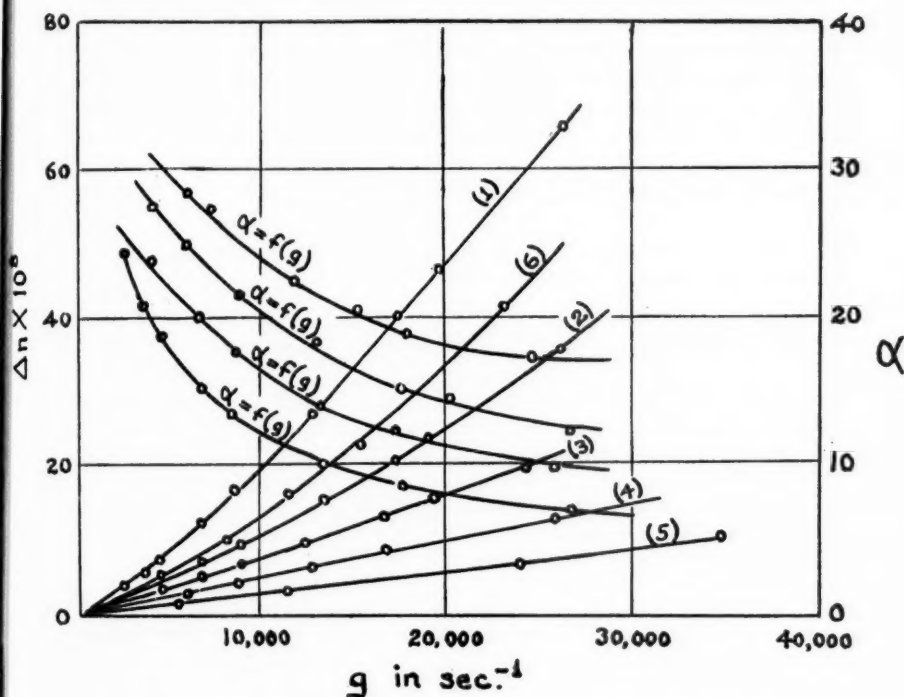


FIG. 6.—Dependence of the double refraction of Vistanex in tetralin on the temperature.

1. $t = 12.5^\circ$, $C_m = 0.401$, 13.04, $\eta = 0.306$,	2. $t = 31.4^\circ$, $C_m = 0.396$, 13.8, $\eta = 0.215$
3. $t = 48.5^\circ$, $C_m = 0.391$, 13.3, $\eta = 0.16$,	4. $t = 68.2^\circ$, $C_m = 0.386$, 13.2, $\eta = 0.122$
5. $t = 88^\circ$, $C_m = 0.380$, 13.8, $\eta = 0.097$,	6. $t = 12.5^\circ$, Solution after prolonged warming

The corrected values of Z also decrease with the temperature; however, it may be assumed that a rise in temperature of 30–40° C (doubling of η) does not change significantly the dynamic optical constant of the solution.

Signer⁵ arrived at the same results from a study of the temperature dependence Δn of a solution of polystyrene within a narrower temperature range (up to 40° C).

Hence, if we substitute a solvent of different viscosity, the change in the viscosity η_0 cannot by itself modify essentially the value of Z . This fact is very important in comparing the effects obtained in various solvents.

The value of Z , therefore, may be used as a criterion of the double refraction of a flowing liquid, and may be regarded as the dynamic optical constant.

THE DYNAMIC OPTICAL EFFECT IN VARIOUS SOLVENTS

The possibility of applying existing theories depends on whether it is possible, on the basis of experimental data, to draw any conclusions regarding the nature of the double refraction observed. Is the latter the result of orientation of optically anisotropic particles (the anisotropic effect), or is it related to their elastic deformation (elastic effect), and to what extent is the effect limited by the shape of the particles (double refraction effect)?

The influence of the shape of the particles might be determined by an investigation of the double refraction of rubber in solvents with various refractive indices.

As is known, in a liquid with refractive index n_0 and containing rod-shaped particles, uniformly orientated, and themselves having a refractive index n , the double refraction is, according to Wiener⁷:

$$n_1^2 - n_2^2 = \frac{\Omega(n^2 - n_0^2)^2}{(\Omega + 1)n_0^2 + (1 - \Omega)n^2} \quad (1)$$

where Ω is the portion of the volume occupied by suspended particles.

If the concentration is not high ($\Omega \ll 1$), then:

$$n_1^2 - n_2^2 = 2n_0\Delta n = \frac{\Omega(n^2 - n_0^2)^2}{n^2 + n_0^2} \quad (2)$$

Evidently, for the substance in solution ($n = \text{const.}$) the curve representing the double refraction Δn as a function of n_0 is a parabola, which passes through the origin of the coordinates (when $n = n_0$, the effect is 0).

If the particles are optically anisotropic when $n = n_0$, the double refraction does not equal 0, and the parabola passes through a minimum. The location of this minimum on the axis Δn characterizes the particular double refraction of the particles, which may be either positive or negative, *e.g.*, as in the case of polystyrene.

We measured the double refraction of solutions of Vistanex (milled 60 minutes) in six solvents having various refractive indices. The results are shown in Table III.

The value of Z corresponding to the velocity $17,000 \text{ sec.}^{-1}$ was calculated for each solution. The average value for each solvent appears in the last column of Table 3. It will be seen that the dynamic optical constants for various solvents differ markedly.

If the values of Z are plotted, with n_0 , the index of refraction of the solvent, as the abscissa, definite conformity with well established principles is observed. The points lie on the curve, and have a minimum near an n_0 value of 1.48. Thus the shape of the rubber particles in a solution has a definite influence on the optical anisotropy of the latter.

There is no doubt, however, that the double refraction observed in a flowing liquid involves not only the double refraction resulting from the shape of the particles, but the optical anisotropy of the particles, inasmuch as the $Z = f(n_0)$ curve does not touch the abscissa at any point. Polyisobutylene has an index of refraction, n , of 1.5; therefore it was to be expected that the minimum of the curve would lie at an n_0 value of 1.5. The fact that it shifts toward a smaller

TABLE 3
VISTANEX, MILLED 60 MINUTES

Solvent	Index of refraction n_0	Viscosity of solvent η_0	Molecular concentration C_m	Specific viscosity η_{sp}/C_m	Absolute viscosity η_{abs}	$\frac{\Delta n}{g} \times 10^{11}$	$\frac{\Delta n}{\rho C_m \sqrt{\eta_0}} \times 10^5$	$\frac{\Delta n}{\rho C_m \sqrt{\eta_0}} \times 10^5 \left[\frac{\Delta n}{\rho C_m \sqrt{\eta_0}} \times 10^5 \right]_{ave.}$
Naphtha < 100° C	1.412	0.00555	0.2	2.86	0.0214	1.5	6.75	5.95
Naphtha < 100° C	1.412	0.00555	0.3	7.22	0.0456	2.84	6.05	5.95
Naphtha < 100° C	1.412	0.00555	0.15	1.98	0.0165	0.786	5.55	5.95
Naphtha < 100° C	1.412	0.00555	0.4	12.33	0.0731	4.44	5.5	5.95
Benzene	1.50	0.0073	0.2	1.56	0.0187	0.698	3.02	3.28
Benzene	1.50	0.0073	0.3	3.56	0.0333	1.58	3.46	3.28
Benzene	1.50	0.0073	0.4	7.62	0.063	2.88	3.37	3.28
Carbon tetrachloride	1.467	0.01209	0.193	3.55	0.0551	1.77	3.55	3.52
Carbon tetrachloride	1.467	0.01209	0.289	7.92	0.1017	3.59	3.65	3.52
Carbon tetrachloride	1.467	0.01209	0.386	14.5	0.1873	5.88	3.36	3.52
Chloroform	1.451	0.00946	1.1888	1.92	0.0276	0.882	2.89	3.08
Chloroform	1.451	0.00946	0.2831	4.59	0.0529	2.15	3.39	3.08
Chloroform	1.451	0.00946	0.3775	7.97	0.0848	3.18	2.97	3.08
Tetralin	1.548	0.0234	0.201	2.81	0.0892	4.59	5.0	5.58
Tetralin	1.548	0.0234	0.267	4.12	0.12	6.38	4.53	5.58
Tetralin	1.548	0.0234	0.151	1.74	0.064	3.7	6.35	5.58
Tetralin	1.548	0.0234	0.10	0.93	0.0451	2.09	6.46	5.58
Naphtha (100-120°)	1.42	0.006	0.33	8.24	0.063	3.0	4.4	4.4

value of n_0 , and that there also is a marked scattering of points, must be attributed to the influence of the interaction between molecules of the solvent with molecules of the dissolved polymer. It is probable also that the marked tendency of the rubber micelles to swell in various solutions plays an important part. Particularly does a small Z value contribute significantly to a displacement of the curve, which is evident in the solution of Vistanex in chloroform. It should be noted that solutions of rubber in this solvent show abnormally low relative viscosities.

By using the formula of Wiener, it is possible to calculate the maximum double refraction due to shape in a solution of polyisobutylene ($n = 1.5$) in various solvents, with complete orientation of all micelles.

For example, when C_m was 0.3 ($\Omega = 1.68 \times 10^{-3}$, the following values were obtained:

n_0	1.410	1.420	1.451	1.467	1.500	1.548
$\Delta n_{\max} \times 10^6$	9.64	7.56	2.62	1.25	0.00	2.5

On the other hand, for a solution of Vistanex with a C_m value of 0.3 in naphtha ($n = 1.41$), when g was 34,000 sec.⁻¹ the double refraction Δn was 1.10^{-6} .

It is seen from the graph in Figure 7 that half of the observed effect in naphtha is due to the double refraction which depends on shape, and which consequently equals 0.5×10^{-6} , whereas the maximum possible value of Δn is 9.64×10^{-6} . Therefore the double refraction resulting from the shape of the particles at the highest velocity gradients is merely 5 per cent of the double refraction corresponding to complete orientation of the particles.

Similar investigations were conducted with a plasticized butadiene-styrene

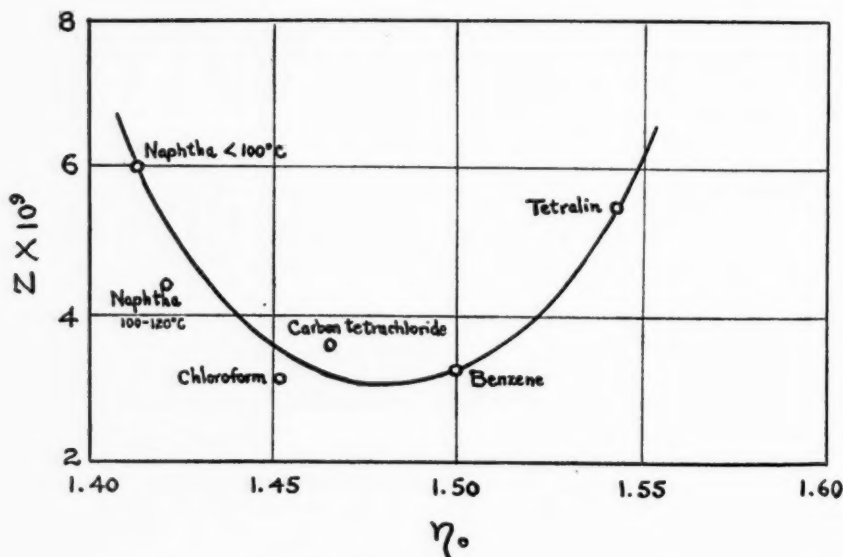


FIG. 7.—Vistanex milled 60 minutes.

$$Z = \frac{\Delta n}{g C_m \sqrt{\eta \eta_0}} = f(n_0)$$

polymer. The results, shown in Figure 8, show the relation: $Z = f(n_0)$. The graph shows a significantly wider scattering of points than for isobutylene. The data for chloroform solutions were particularly irregular, and consequently are omitted from the graph. The fact that a technical sample which had not been specially purified, and therefore contained a considerable quantity of colloidal impurities, was used, accounts for the scattering. A contributing factor may also have been the fact that the sample was a mixed polymer.

However, in spite of the considerable deviations of the individual points, the minimum of the $Z = f(n_0)$ curve lies in the region of larger n_0 values than the minimum of isobutylene. This was to have been expected in view of the fact that the index of refraction of Buna-S is 1.53.

Thus, as for isobutylene, the dynamic double refraction of Buna-S solutions is an effect not only of the double refraction resulting from the shape of the particles, but also of the optical anisotropy of the particles. In addition, part of the dynamic optical constant corresponding to this anisotropy equals 4×10^{-9} , as is evident from the graph in Figure 8.

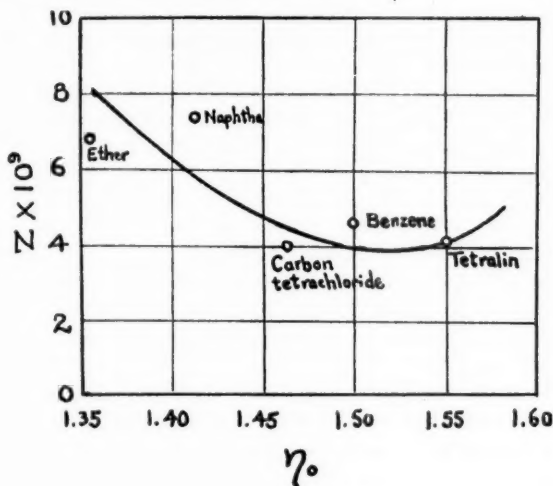


FIG. 8.—Buna-S. $Z = f(n_0)$.

ANISOTROPY OF PARTICLES IN A FLOWING LIQUID

After having determined that the particles of solutions of two samples of synthetic rubber when under flow were optically anisotropic, we attempted to ascertain whether this anisotropy was an inherent property, or was a result of mechanical strain. Information on this question can be obtained by comparative measurements of the double refraction Δn and the angle of extinction α .

Taking into account the influence of the inherent anisotropy and the shape of the particles, as the theory requires and as experiments confirm with colloidal solutions containing solid crystalline particles, with significant deviation of the angle of extinction from 45° , the curve $\Delta n = f(g)$ should show a tendency to saturation when $\alpha = 0$.

On the contrary, in the presence of elastic double refraction, as theory demonstrates⁸, even with angles of extinction which differ only slightly from

zero, the relation: $\Delta n = f(g)$, does not change substantially, and the double refraction remains proportional to the velocity.

In all the cases investigated in the present work, even when g was 50,000 sec.^{-1} , the relation: $\Delta n = f(g)$, remained either rectilinear for samples with large molecular weights or was a curve with concavity upwards (Oppanol, Vistanex and natural rubber).

Meanwhile, for the same velocities of flow, the angles of extinction in most cases differed from 45° by 10° , and in certain cases it reached zero when g was very small (Oppanol and Vistanex).

Therefore, without recourse to calculation, it may be concluded that the double refraction observed in a flowing liquid is, at least in part, governed by the strain in the particles (elastic effect).

The theory of oriented double refraction, including the observed effect of the inherent anisotropy of the particles, gives a direct relation between the measured angle of extinction α and the corresponding double refraction Δn , expressed as the part of the maximum possible effect which might be observed with completely parallel orientation of all particles. Evidently, the maximum effect equals $\Omega(n_1 - n_2)$, where Ω is the part of the volume occupied in the solution by the particles, and $n_1 - n_2$ is the inherent double refraction of a particle of the substance. The relation: $\Delta n / [\Omega(n_1 - n_2)] = f(\alpha)$ was calculated by Kuhn⁹, and is shown in the form of a curve in his paper.

By comparing the value of Δn determined experimentally with its corresponding angle α , and using the curve of Kuhn, it was possible to compute the inherent anisotropy of particles, $n_1 - n_2$.

When estimated in this way, the values of $n_1 - n_2$ do not represent the true optical anisotropy of the particles, since they are the sum of the double refraction resulting from both shape and strain.

The latter should be taken into account in view of the fact that its value must increase with increase in the hydrodynamic influence sustained by a particle during flow (proportional to the product, $\eta_0 \sqrt{X} \cdot g$). A comparison of the values of $n_1 - n_2$, obtained at various velocities, shows that in all cases $n_1 - n_2$ increases with increase in $\eta_0 \sqrt{X} \cdot g$. This indicates beyond doubt the existence of elastic anisotropy. This is shown graphically in Figure 9, where some observed values of $n_1 - n_2$ are represented as a function of $\eta_0 \sqrt{X} \cdot g$.

Moreover, it appears that, for a given sample in a given solvent, the points obtained for solutions of various concentrations lie on the same $n_1 - n_2 = f(g\eta_0 \sqrt{X})$ curve.

Warming of the solution to 50°C does not change the character of the curve, but by heating to 68° , the curve is displaced downwards as a result of the irreversible changes in the solution which were mentioned earlier.

To various samples of rubber with the same $g\eta_0 \sqrt{X}$ value correspond, generally speaking, various $n_1 - n_2$ values. Solutions of the same rubber in various solvents give various $n_1 - n_2 = f(g\eta_0 \sqrt{X})$ curves in accord with the marked influence of the double refraction caused by shape (Figure 9).

In principle it is possible to exclude the effect of tension in measuring n and α for very small $g\eta_0 \sqrt{X}$ values. However, it is actually impossible to do this, since the accuracy in determining α when η is small and consequently when Δn also is small, is not at all good.

Of course, it is possible to extrapolate the $n_1 - n_2 = f(g\eta_0 \sqrt{X})$ curves as far as the intersection with the ordinate; however, this extrapolation is some-

what arbitrary, since in the region of small g values, the curvature increases. In every case investigated, the extrapolated curves intersected the ordinate axis higher than zero.

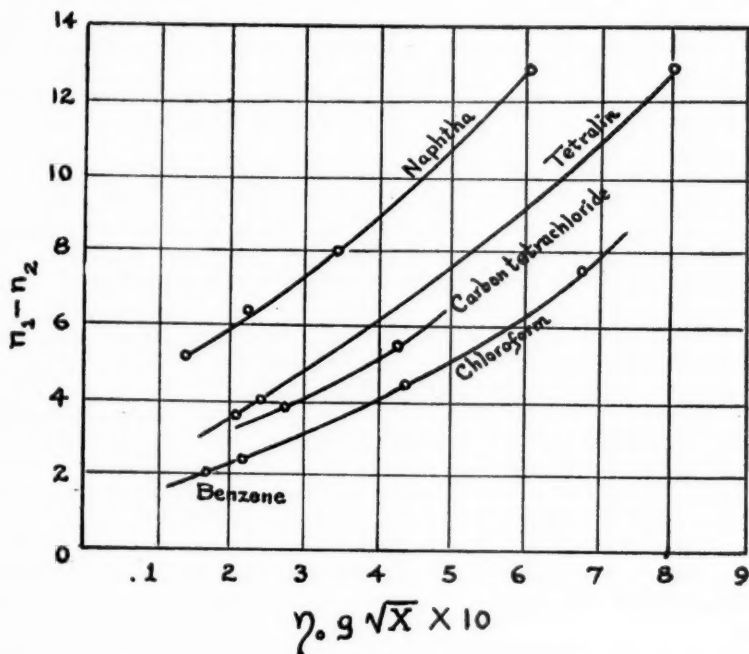


Fig. 9.—Vistanex, milled 60 minutes. Anisotropy of particles with various g values.

To take into account the anisotropy of shape in the $n_1 - n_2$ value, it is necessary to use the solvent for which the $Z = f(n_0)$ curve (see Figure 7) is a minimum.

In our work Vistanex was used (Figures 7 and 9), in which case the minimum Z values were obtained in benzene and chloroform. Unfortunately, with benzene, it was possible to calculate only one $n_1 - n_2$ value corresponding to $g\eta_0\sqrt{X} = 1.7 \times 10^{-2}$; therefore extrapolation of this value was impossible. By extrapolation of the $n_1 - n_2$ curve in Figure 9 for chloroform, a limiting value of the order of magnitude of 10^{-5} was obtained. For other rubbers in different solvents, extrapolation gave $n_1 - n_2$ values of the same order.

Of the rubbers which were studied, the inherent anisotropy of the particles, *i.e.*, the normal double refraction of the substance of which they are composed, did not exceed 5×10^{-5} , and in many cases was considerably less than this amount.

ANISOTROPY OF PARTICLES IN AN ELECTRIC FIELD

If a particle is in itself optically anisotropic, it should also exhibit anisotropic polarity in a static electric field. Besides this, the dielectric anisotropy is somewhat more optical, since polarity in a static field includes electronic displacement and displacement of the heavy particles (ions) in the molecule,

whereas polarization in the field of light waves (visible range) leads only to electronic displacement. However, the difference between optical and total polarity is small, and ordinarily does not exceed 10 per cent. Therefore, in further approximate calculations no distinction is made between them.

As is known, measurement of the electrooptical effect of Kerr in a system of noninteracting particles may serve as a method of determining their electrical (optical) anisotropy.

If the particles are nonpolar, the amount of double refraction in an electrical field E is:

$$\Delta n = \frac{2\pi}{3kT} \cdot \frac{(n_0 + 2)^2}{45n_0} \cdot (b_1 - b_2)^2 \cdot E \left(\frac{\epsilon + 2}{3} \right)^2 N \quad (3)$$

Here n_0 is the index of refraction, of the solvent, ϵ its dielectric constant, N the number of particles in one cc., and $b_1 - b_2$ the electrical (optical) anisotropy of a particle (for simplicity it is assumed that the particle has a symmetrical electrical axis).

We may apply the equation derived in this way to electric double refraction in rubber solutions, inasmuch as polymerization leads to the formation of macromolecules not having a dipolar moment.

If the degree of polymerization is ν , and if it is assumed that in the solution we are dealing directly with molecules of rubber, each of which contains ν molecules of the monomer, then:

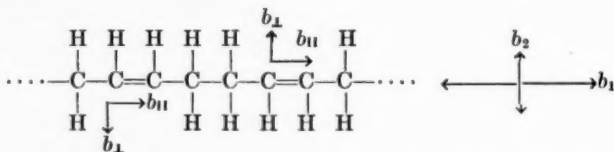
$$N = \frac{\rho}{M} \cdot \frac{N_L}{\nu} \cdot C_0$$

where ρ is the density of the polymer, C_0 its concentration in the solution (grams per cc.), M the molecular weight of the monomer, and N_L , Loschmidt's number.

Further, if it is assumed that polymerization leads to the formation of rigid linear macromolecules, in which separate bonds (monomer molecules) are arranged in normal order, the optical anisotropy of a particle may be considered to be equal simply to the sum of those values for basic molecules:

$$b_1 - b_2 = \nu(b_{11} - b_{1\perp})$$

For example, if polymerization in a butadiene chain proceeds in such a way that the molecules of the monomer are in 1,4-position, the long axis of a molecule of butadiene (axis of optical symmetry) is:



coincides with the axis of symmetry of a macromolecule of polybutadiene, which must lead to additive optical anisotropy.

If polymerization leads to the formation of a branched polymer, *i.e.*, proceeds partly according to a 1,2-linking¹⁰, then, there will be no such additive effect. In this case:

$$b_1 - b_2 = \frac{\nu}{S} (b_{11} - b_{1\perp}),$$

where the factor S represents the decrease in anisotropy of a macromolecule as a result of branching.

However, the factor S may have also another value. If during polymerization even a short linear chain is formed, and if in addition it is sufficiently flexible, then the molecules in solution will have the form of sharply curved threads; or even of balls, which may lead to a sharp decrease in the anisotropy. In such a case S will be a measure of the deviation of a molecule from a rigid linear form and a measure of its curvature and flexibility.

Introducing into Equation (3) the N values and $b_1 - b_2$ values of a solution of polymer:

$$\Delta n = \frac{2\pi}{3kt} \cdot \frac{(n_0^2 + 2)^2}{45n_0} \cdot \frac{\rho}{M} N_L C_0 \left(\frac{\epsilon + 2}{3} \right)^2 E^2 S^2 \nu (b_{11} - b_{12})^2 \quad (4)$$

The electric double refraction of a solution of butadiene-styrene polymer in carbon tetrachloride ($C_0 = 3.5$ per cent) was determined. The usual method for studying the Kerr effect was used, with a constant electric field having an intensity of 130 c.g.s. units. The compensator was equipped with a mica plate (0.02λ), and carbon tetrachloride was chosen as the solvent because of its low conductivity and insignificant Kerr constant.

A constant electrical field with an intensity of 130 c.g.s. was used. The electrical double refraction of the pure solvent was first measured. As compensation for the effect in the field $E = 130$ CGSE, the compensator had to be turned to the angle $\Delta\phi = 1^\circ 1' \pm 5'$, which corresponded to the double refraction:

$$\Delta n_{CCl_4} = 5.8 \times 10^{-9} \pm 0.5 \times 10^{-9}$$

The accuracy in determining the angle of compensation in the solution was less, due to discoloration and insufficient purity of the solution (the sample had not been specially purified or decolorized). In the field E of the same strength, $\Delta\phi = 2^\circ 16' \pm 30'$, which corresponded to the value:

$$\Delta n_1 = 13 \times 10^{-9} \pm 3 \times 10^{-9}$$

Hence, the double refraction, which was governed by the presence of rubber in the solution in a field of $E = 130$ CGS was:

$$\Delta n = \Delta n_1 - \Delta n_{CCl_4} = 7 \times 10^{-9} \pm 3 \times 10^{-9}$$

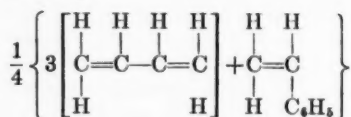
Since the solution was not specially purified, and therefore, probably contained impurities which affected the observed effect, it can merely be asserted that the double refraction Δn resulting from orientation in a field of particles of pure polymer, does not exceed

$$\Delta n < 7 \times 10^{-9} \pm 3 \times 10^{-9} \quad (5)$$

On the other hand, we may estimate the effect which is to be expected in accordance with Equation (4).

The structural formula of butadiene-styrene polymers is unknown; by measuring the index of refraction of rubber it was possible to prove that, in a mixed polymer, there must be three molecules of butadiene for each molecule of styrene. Therefore, provisionally, the formula for an "average" molecule may

be represented in the following form:



in accordance with which the molecular weight of the monomer is 66.

The optical anisotropy of a molecule may be estimated in the following manner. The variation in polarities of butadiene may be considered to be double the anisotropy of ethylene, which is 20×10^{-25} . As far as styrene is concerned, it is known that its double refraction in a magnetic field is twice that of benzene, a value which agrees with our measurements. One may assume, then, that the optical anisotropy of its molecule is twice that of benzene, which is 60×10^{-25} .

Thus, the optical anisotropy of an "average" base molecule of butadiene-styrene polymer is:

$$b_{11} - b_{\perp} = \frac{1}{4}[3(20 \times 2) + 2 \times 60] \times 10^{-25} = 60 \times 10^{-25}$$

Therefore by placing the value in Equation (4):

$$n_0 = 1.4; \quad \rho = 1; \quad M = 66; \quad E = 130; \quad kT = 5 \times 10^{-14}; \\ \nu = 10^3; \quad C_0 = 3.5 \times 10^{-2}; \quad \epsilon = 2.5; \quad b_{11} - b_{\perp} = 60 \times 10^{-25}$$

the value of the expected effect is obtained:

$$\Delta n = 6.5 \times 10^{-6} \cdot \frac{1}{S^2}$$

Hence, if a molecule of polymer in solution is conceived to have a rigid structure, in which the molecules of the monomer form a linear chain, S must equal 1, from which we have $\Delta n = 6.5 \times 10^{-6}$, that is, a quantity 1000 times larger than what was actually observed experimentally.

Comparing the theoretically obtained value of Δn with the left part of the inequality (5) we find:

$$S^2 > 930, \quad \text{or} \quad S < 30; \quad \frac{1}{S} < 0.03$$

Experiments in an electrical field indicate that the true optical anisotropy of the particles of the particular polymer which was examined was less than 3 per cent of the value which it would have had to have without bending and without any branched molecules.

Besides, it must be remembered that this is only the upper limit of this value, and with purified solutions, it would in all probability be considerably less.

SHAPE OF PARTICLES IN SOLUTION

We have seen that, on the basis of experiments on double refraction in a flowing liquid, it is possible to estimate the true double refraction of a polymeric substance from which the particles in solution are formed. In no case did this value exceed 5×10^{-5} .

The double refraction of the least optically anisotropic quartz crystal is 0.01; it is usually considerably more in organic crystals; in fact it reaches

values of almost unity. Consequently the anisotropy of rubber particles is at least 10^3 less than that of normal crystals. This means that there is no orderly arrangement of molecules in the substance comprising the particles.

It is not difficult to calculate the double refraction, for example, of butadiene rubber, in which the molecules are in complete parallel orientation.

Using the equation of Mosotti-Clausius, we have approximately:

$$n_e - n_o = \frac{4}{3} \pi N_L \cdot \frac{\rho}{M} \cdot \frac{n^2 + 2}{2n} (b_{11} - b_{12})$$

By inserting the corresponding values for butadiene polymer and letting $n = 1.5$; $b_{11} - b_{12} = 40 \times 10^{-25}$, we find that:

$$n_e - n_o = 0.1,$$

that is, a quite normal value for an organic crystal.

The results of the experiments described in the last paragraphs would seem to be an argument against the ideas of Staudinger concerning the structure of particles of a polymer in solution. A particle of rubber in solution cannot be rigid and linear in structure, for it is practically isotropic optically.

The observed double refraction in a flowing liquid is basically a photoelectric effect, at least when g is sufficiently large, and it is partly governed by the shape of the particle.

There are several possible reasons for the appreciable anisotropy in a particle.

(1) An individual particle in solution is a macromolecule of the polymer and is composed of a small linear chain of monomeric molecules (in polymerization union proceeds according to Schemes 1 to 4). However, due to flexibility of the chain (free rotation of the groups around the bonds), the particle has the form of a thread rolled into a ball.

(2) An individual particle in solution is a macromolecule of the polymer. Due to the formation of lateral chains during polymerization (union of the bonds in the 1,2-positions), the molecule is strongly branched, with separate bonds distributed in it "isotropically".

(3) An individual particle in solution is a micelle, composed of associated molecules of the polymer distributed in the micelle isotropically.

It is very probable that actually all three reasons account simultaneously for the anisotropy and geometric form of a particle in a flowing liquid. However, their relative importance in the behavior of various rubbers may differ.

These factors are, for example, of fundamental importance in the case of high-molecular polymers of the types of natural rubber, Oppanol, Vistanex, and polystyrene. In these cases the departure from proportionality between Δn and g should be ascribed to a fundamental change in the form of the particle in the flowing liquid, i.e., an elongation due to unravelling.

On the contrary, this effect may not have any great significance in solutions of butadiene polymers, the molecules of which are extensively branched, for this should favor a strengthening of their geometric form. In this case the shape of the molecule is governed almost wholly by the extent of its branching.

As to the possibility of formation of micelles, it does not seem likely that association of molecules may alter radically the shape of the particles. In the first place, since rubber molecules are nonpolar, their power of association is negligible, and cannot lead to the formation of large and stable micelles capable

of surviving in liquids flowing at high velocities. In the second place, due to absence in the molecules of concentrated charges, these forces might be merely a scattered part of Van der Waals interaction, and therefore they are controlled by the surface area of the interacting molecules, and consequently by their shape. Therefore it would be expected that the shape of the micelles which are formed would not be independent of the shape of the associating molecules; more extended molecules in association should lead to more elongated micelles. Therefore, by defining the shape of particles in solution, we directly or indirectly characterize the shape of the macromolecules of the polymer as well.

The shape of particles may be determined by means of data on the double refraction of a flowing liquid. Indeed, if we exclude the effect of double refraction of shape by selecting a solvent with a suitable index of refraction, the measured Δn will be the double refraction of strain, and, consequently, may with the aid of Kuhn's theory⁸ be correlated with the shape of the particles.

According to Kuhn, for small velocities, in which the angle of extinction differs appreciably from zero, double refraction of strain is expressed by the equation:

$$\Delta n = \Omega \cdot \frac{A^2}{B^2} \cdot \frac{\eta \Delta \epsilon}{8} \cdot g \quad (6)$$

Here Ω is the volume in the solution that is occupied by the dissolved polymer. Then:

$$\Omega = \frac{MC_m}{10^3 \rho}$$

A and B are the longitudinal and transverse dimensions of the particles in solution, and $\Delta \epsilon$ the coefficient of optical elasticity of the substance composing the particles, which is numerically equal to the anisotropy set up in the substance by a tension of 1 dyne per sq. cm.

To utilize Equation (6) the factor η must be replaced by a "microscopic" coefficient of viscosity $\eta_1 = \eta_0 \sqrt{X}$. Observing further that:

$$\frac{\Delta n}{C_m g \eta_0 \sqrt{X}} = Z$$

we find:

$$\frac{A}{B} = \sqrt{\frac{8 \rho Z \times 10^3}{M \Delta \epsilon}} \quad (7)$$

Thus, the ratio of the longitudinal and transverse dimensions of the particle is represented directly by the dynamic optical constant Z .

In addition, to exclude double refraction of shape, the value of Z must be obtained by measurement in the solvent. This value corresponds to the minimum of the curve of Figures 7 and 8,

Unfortunately, measurements were carried out only with Vistanex and a Buna-S polymer. For these the relation, A/B , may be calculated.

The indices of refraction of other types of synthetic rubber, except polychloroprene, are close to 1.5. Therefore in cases where measurements are conducted in a solvent having a different index of refraction, the effect of shape was excluded by using the graph in Figure 7, which is of course not wholly justified, for it was not certain that the influence of the shape of the particles of all rubbers was the same as that of Vistanex particles. For butadiene-styrene polymers Figure 8 was used.

The Z elasticity values corresponding to electric double refraction obtained in this way (disregarding the inherent anisotropy of the particles) are given in Table 4.

TABLE 4
MOLECULAR WEIGHT AND SHAPE OF PARTICLES OF VARIOUS POLYMERS

Type of rubber	$\mu \times 10^{-3}$	$Z_{elast} \times 10^9$	$(A/B) \times 10^3$
Polymers of isoprene			
Natural unmilled	100	37.00	4.67
Synthetic No. 44	35	3.73	1.48
Synthetic No. 52	26	2.54	1.22
Polymers of isobutylene			
Oppanol	165	51.0	6.04
Oppanol, milled	30	1.6	1.07
Vistanex	75	5.75	2.03
milled 60 min.	45	2.8	1.42
180 min.	38	2.22	1.26
Polymers of butadiene (gas process)			
No. 3891	38	2.1	1.25
2893	38	2.02	1.23
3894	38	1.95	1.21
3895	38	2.15	1.26
3896	38	2.15	1.26
Polymers of butadiene			
Gas process			
No. 3904	38	2.12	1.25
1340	38	2.05	1.22
5418	28	1.62	1.10
0610	29	1.52	1.06
Rod process			
No. 2608	27	1.36	1.01
23333	20	1.44	1.07
Freeze-resistant			
No. 8123/94	25	1.97	1.21
0641	28	1.98	1.22
6	30	2.44	1.35
8123/107	23	2.0	1.22
Latex			
No. 33890	18	1.26	1.3
76	14	1.81	1.14
2746	11	1.31	0.985

For calculating A/B with the aid of Equation (7), it is necessary to know the optical elasticity $\Delta\epsilon$ of the polymers analyzed.

In our laboratory, the apparatus for the investigations of double refraction of stretched films of polymer was assembled by O. N. Traneznikova, who determined the $\Delta\epsilon$ values of different types of rubbers. In all cases the sign of the double refraction coincided with the effect observed in a solution of the same polymer (positive effect), and differed insignificantly for various samples. For example, for butadiene rubber, $\Delta\epsilon$ was 1.7×10^{-11} ; for Oppanol, it was 1.19×10^{-11} ; and for natural rubber, it was 2.4×10^{-11} . Apparently no great mistake was made in taking for all rubber investigated an $\Delta\epsilon$ value of 2×10^{-11} .

The A/B values obtained by means of Equation (7) are given in the fourth column of Table 4. The second column gives the molecular weights measured

viscometrically. It is evident that the A/B values of the various samples lie within the limits of 100 to 600, that is, several times less than the value which this relation would have if the molecules were rod-shaped, in accordance with the views of Staudinger. For example, Oppanol ($\mu = 165 \times 10^3$ and degree of polymerization $= \nu = 3 \times 10^3$) to agree with Staudinger, would have to have an A/B value of approximately 300, that is, 5 times greater than that actually found. On the other hand, by comparing the A/B values within one group of rubbers, it is found that, for polymers differing only in molecular weight, the greater the value of A/B , the higher the molecular weight. In addition to the data in Table 4, the graphs in Figures 10, 11 and 12 give evidence in support of

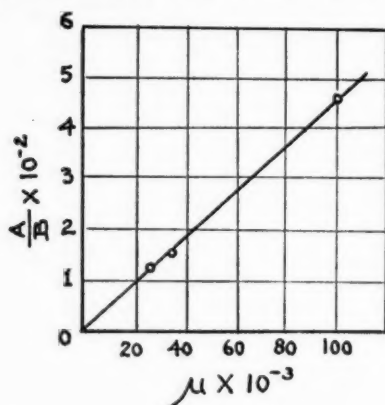


FIG. 10.—Dependence of the shape of a particle on the degree of polymerization. Polyprenes.

this. Accordingly, during polymerization, the growth of the chain proceeds faster in the direction of its length than in a transverse direction.

Noteworthy is the great decrease of A/B brought about by milling Oppanol, which is a linear polymer of high molecular weight. Evidently the extended shape of the particles gives them a greater tendency to sever (relative shortening) when milled than is the case of polymers having branched molecules.

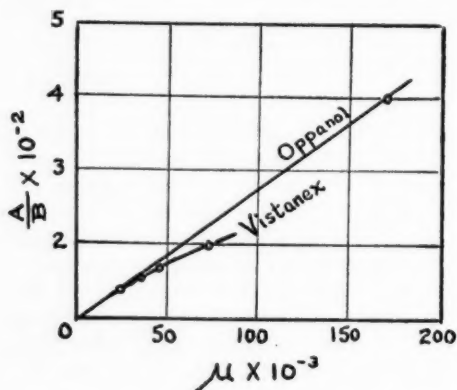


FIG. 11.—Dependence of the shape of a particle on the degree of polymerization. Polyisobutylenes.

Turning to a comparison of the results with butadiene polymers prepared by means of various methods, it is seen that latex rubbers differ from those prepared in the gas phase and those prepared by the rod method by a more extended shape of particle, since for the same molecular weight the quantity A/B in the first case is greater than for the second (see Figure 12).

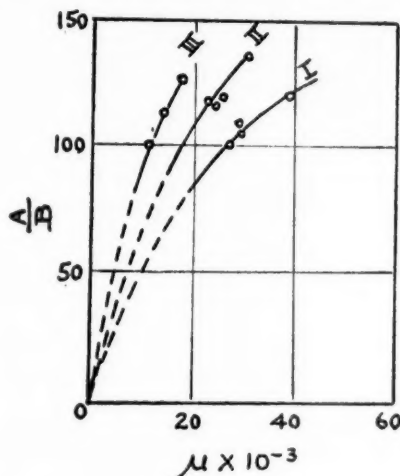


FIG. 12.—Dependence of the shape of a particle on the degree of polymerization. Polybutadiene. I, Gas process; II, Resistant to freezing; III, Latex.

No essential difference was noticed in the shape of the particles of polymers prepared by the gas and rod methods. Freeze-resistant rubbers showed higher values than did ordinary synthetic rubbers made by methods other than the rod method. It would be profitable to compare the data obtained in the present work with data on the extent of branching of molecules of certain butadiene polymers by the method of ozonization. The latter unpublished work was furnished the present authors by A. A. Vasiliev.

Comparative data are presented in Table 5, where, in addition to A/B values, the percentage of bonds with a free vinyl group are given. These will serve as a measure of the extent of branching of the molecules.

TABLE 5

COMPARATIVE DATA ON THE SHAPE OF MOLECULES OBTAINED BY THE METHOD OF DOUBLE REFRACTION IN A FLOWING LIQUID AND BY THE METHOD OF OZONIZATION

No. of Sample	$\frac{A}{B} \times 10^{-2}$	Number of bonds with a free vinyl group (percentage)
2608	1.01	49
34333	1.07	49
0610	1.06	40
0641	1.22	31
33890	1.30	31

We are convinced of the agreement between the two methods in that they show that molecules which have relatively little branching have as a rule, large A/B values.

SUMMARY

The work which is described in the present paper is concerned with the development of a method for measuring the double refraction of a flowing liquid, with particular attention to a study of the structure of polymers.

The dependence of double refraction and of the angle of extinction on the velocity of flow of solutions of thirty samples of synthetic rubber through a wide range of velocities was studied.

For linear polymers having high molecular weights, the relation: $\Delta n = f(g)$, shows, when represented graphically, an ascending concave curve. This relation is rectilinear for all polymers whose molecular weights lie within the usual range. In all cases investigated, the angle of extinction lay within the limits of 45° and 0° .

The dynamic optical constant which characterizes the double refraction of rubber was established experimentally. This dynamic optical constant was calculated for all samples of rubbers which were studied. Three effects on the double refraction of a solution of a polymer during flow were distinguished experimentally: (1) the effect of the shape of the particles; (2) the effect of the anisotropy of the particles; and (3) the elastic effect.

The double refraction of solutions of synthetic rubbers in an electric field was investigated with a view to determining the anisotropy of the molecules of the polymers.

On the basis of the experimental data it is concluded that the double refraction of a flowing rubber solution is fundamentally influenced by the effect of tension.

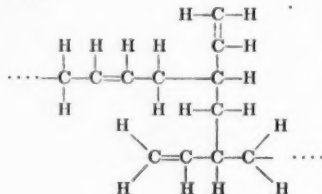
The theory of Kuhn and the experimental data obtained in the present work were utilized to calculate the relation between the transverse and longitudinal dimensions of all the rubbers which were studied.

ACKNOWLEDGMENT

This work is a continuation of earlier work by the same authors¹, and was carried out in the plant of the S. B. Lebedev factory, making Type B synthetic rubber, with the aid of workers and laboratory personnel under the leadership of A. I. Urzhenko, Chief of the Physico-Chemical Laboratories, and N. N. Mikhailov, Chief of the Physical Laboratories, to whom the authors express appreciation for their interest and participation in the work.

REFERENCES

- ¹ Tsvetkov and Petrova, *J. Tech. Phys.* (U.S.S.R.), **12**, 423 (1942).
- ² Signer, *Trans. Faraday Soc.* **32**, 296 (1936).
- ³ Freundlich, *Z. physik. Chem.* **114**, 161 (1924).
- ⁴ Boeder, *Z. Phys.* **75**, 258 (1932); Kuhn, *Z. physik. Chem.* **161**, 1, 427 (1932).
- ⁵ Signer, *Z. physik. Chem.* **165**, 161 (1933).
- ⁶ Tsvetkov and Michailov, *Acta Physicochimica U.S.S.R.* **18**, 77 (1938).
- ⁷ Wiener, *Ber. Sachs. Ges.* **61**, 113 (1933).
- ⁸ Kuhn, *Z. physik. Chem.* **161**, 427 (1932).
- ⁹ Kuhn, *Kolloid-Z.* **62**, 269 (1933).
- ¹⁰ The structure in this case would be:



GAS PERMEABILITY AND THE MICROSTRUCTURE OF POLYMERS *

S. A. REITLINGER

At the present time one of the problems of greatest interest in connection with the investigation of the permeability of gases through films of high polymeric compounds appears to be the question of establishing certain general relationships between the structure of a polymer and its quantitative gas permeability.

The existence of a quantitative relationship between the permeability and solubility of a gas in rubber was established by Graham¹, Wroblewski², and Venable and Fuwa³. The manner in which successive sorptions, diffusions, and desorptions of gas in a film of a polymer change with decrease in the concentration gradient of the gas was investigated in connection with studies of the process of penetration by Kayser⁴, Stefan⁵, and Edwards and Pickering⁶.

Investigation of the kinetics of penetration, beginning with the moment of contact of gas with the surface of the film, reveals three separate stages of development.

In the initial period the gas is completely absorbed in the film, and desorption of the gas from the reverse side of the film is not observed. The next period is characterized by a progressive increase in the rate of passage of gas through the film. Finally, in the third period, this rate becomes constant⁷.

In the final stage the process is governed by Fick's Law, which is related to Henry's Law for the solubility of gases in polymers ($c = Sp$):

$$Q = -DS \frac{\Delta p}{L} t \quad (1)$$

where Q is the quantity of gas passing in time t through a unit of transverse section with the effective pressure gradient $\Delta p/L$, D is the diffusion coefficient, and S is the coefficient of gas absorption by the polymer (or solubility of the gas in the polymer). If t and $(\Delta p + 1)/L$ are in equivalent units, the quantity Q is the gas permeability of the polymer.

The coefficients D and S , which are conditionally related to the quantitative permeability, can be definitely determined by the application of Fick's general differential equation:

$$dc/dt = D(\partial^2 c / \partial x^2) \quad (2)$$

Integrating this equation between definite limits:

$$c = f(x') \quad \text{for} \quad t = 0, \quad x' < L$$

and at the limiting conditions:

$$c = c' \quad \text{for} \quad x = 0 \quad \text{and} \quad c = c_2 \quad \text{for} \quad x = 1.$$

* Translated by H. K. Livingston from the *Zhurnal Obshchei Khimii* (Journal of General Chemistry, U.S.S.R.), Vol. 14, No. 6, pages 420-427 (1944).

As was shown by Daynes⁸ this leads to the expression:

$$Q = DS(p/L)(t - L^2/6D), \quad (3)$$

where L is the film thickness.

From a graphical representation of $Q = f(t)$, it is possible to determine the quantity $L^2/6D$ and then to calculate the value of D . The coefficient of sorption can be determined from the known quantities D and Q by means of Equation (1).

In the work of DeBoer and Fast⁹, Sager¹⁰, and Barrer¹¹, it was established that the temperature dependence of permeability is obtained in the form:

$$P = P_0 e^{-E/RT} \quad (4)$$

where P is the permeability and P_0 and E are constants.

Barrer has shown that the temperature dependence of the coefficients D and S also follows the exponential law and that the diffusion of nonpolar gases through polymers can be treated as nonspecific activated diffusion, analogous to the diffusion of gases in glass¹². According to Barrer¹³, nonspecific activated diffusion of gases in polymers depends on the statistical distribution of the free spaces ("holes") in the polymers, as determined by the fluctuations of the separate links in the principal valence chains, since activation energies of "hole" formation are approximately equal to the energies for overcoming intermolecular van der Waals' forces.

The scheme of diffusion given above permits the assumption that the permeability of gases through films depends primarily on the microstructure of the polymers, and on the form, dimensions, interrelations and interactions (the character of the intermolecular bonds) of macromolecular polymers. This dependence was investigated experimentally by determining the permeability, diffusion, and sorption of hydrogen of a series of polymers chosen so as to exhibit variations in molecular weight, in the form of the principal valence chain, and in the nature of the side groups attached to the principal valence chain. The influence of the character of the intermolecular bonds on the mechanism of permeability was investigated by determining the activation energy of permeability of certain polar and nonpolar polymers.

EXPERIMENTAL PART

Hydrogen free from oxygen, which had been obtained electrolytically, was used for the investigation of the gas permeability of films. Hydrogen was chosen as the gas because of its inertness, the convenience with which it can be accurately determined in small quantities, and the practical interest of the results obtained. The hydrogen permeability of films of polymers was determined at $20 \pm 0.2^\circ \text{C}$, using a modification of the apparatus of Daynes¹⁴, as described previously by Reitlinger and Panyanina¹⁵. A reflecting galvanometer with a sensitivity of 3.6×10^{-9} ampere was used for recording.

The coefficients of permeability, diffusion, and sorption of hydrogen were calculated from the data by Equations (1) and (3). Permeability was expressed in cc. of hydrogen per sq. cm. per sec. for a thickness of 1 cm. and a pressure difference of 1 atmosphere; the coefficient of diffusion in sq. cm. per sec., and the coefficient of sorption in cc. of gas per cc. of polymer, for a pressure of 1 atmosphere. It was necessary for experimental reasons to have polymer films with thicknesses of the order of 0.08–0.10 cm. They were obtained by

Sager's method, *i.e.*, by evaporating solutions of polymers cast on stretched cellophane framelets¹⁶.

The residual solvent was removed by exposing the films to a vacuum at 60° C until constant in weight. Polymers subject to oxidation by air were stabilized by the introduction of 0.5 per cent of aldol- α -naphthylamine.

Results of the determination of the quantities P , D , and S (Tables 1 to 4) are given as obtained in ten separate experiments.

TABLE 1
THE HYDROGEN PERMEABILITY OF FRACTIONS OF
POLYSTYRENE AND POLYISOBUTYLENE

Polymer	Molecular Weight by Staudinger	$P \times 10^8$
Polystyrene	110,000	11.20
	23,000	11.30
	9,500	11.60
Polyisobutylene	274,800	5.02
	103,500	5.10
	54,000	5.06
	35,000	5.32

The dependence of permeability on the length of the principal valence chain of the polymer was investigated for films obtained from different fractions of polystyrene and polyisobutylene. The results of these measurements are shown in Table 1.

The influence of the configuration of the principal valence chains on the values P , D , and S was investigated in the case of natural rubber and gutta-percha, which have the same composition but differently constructed macromolecules, and also of films of polybutadiene and copolymers of butadiene with styrene and butadiene with acrylonitrile. The results of these investigations are shown in Table 2.

Finally, data are given in Table 3 for P , D , and S as determined for a group of polymers, which have the same form of the principal valence chain but different side groups. If hydrogen is allowed to penetrate polymers which have chains containing groups of the same or different polarity, it is possible to explain the influence of the energy of the intermolecular bonds on permeability. The low values of permeability of polymers containing polar groups may be due either to a reduction in the number of possible paths of penetration of the hydrogen molecules or to an increase in the activation energy of permeability. To determine which of these possibilities is correct, we measured the activation energies of permeability of hydrogen through films of a series of polymers, as given in Table 4. The activation energy of permeability is calculated from Equation (4), using permeability values determined at 0°, 20°, 30°, and 40° C.

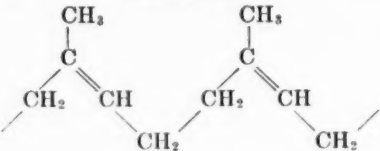
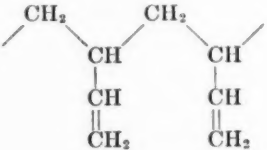
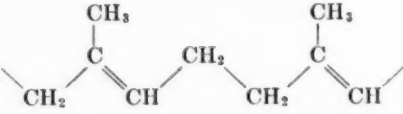
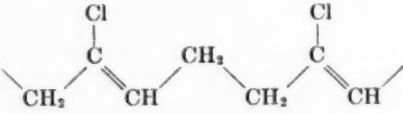
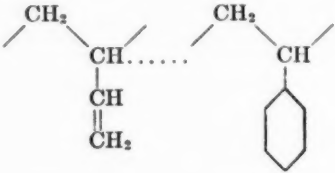
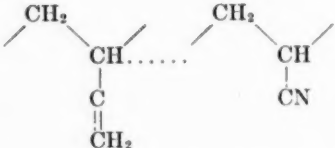
CONSIDERATION OF RESULTS

Let us examine the influence of the different types of microstructure on the gas permeability of polymers, with reference to the experimental data presented above.

(1) *The length of the principal valence chain.*—The variations in the length of the principal valence chain of film-forming polymers given in Table 1 indicate that there is no correlation with permeability. Analogous data have been

TABLE 2

THE INFLUENCE OF THE CONFIGURATION OF THE CHAIN ON THE PERMEABILITY, DIFFUSION, AND SORPTION OF HYDROGEN OF A SERIES OF DIOLEFIN DERIVATIVES

Polymer investigated	Structural Unit	$P \times 10^8$	$D \times 10^4$	$S \times 10^3$
Natural rubber (pale crepe)		30.08	7.23	4.16
Polybutadiene		34.06	8.06	3.96
Gutta-percha (pure hydrocarbon)		9.31	4.29	2.17
Polychloroprene		7.15	3.18	2.25
Butadiene-styrene copolymer		23.67	8.80	2.69
Butadiene-acrylonitrile copolymer		8.91	4.05	2.20

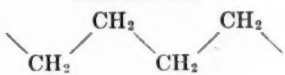
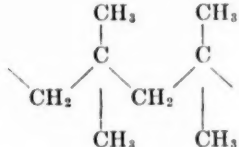
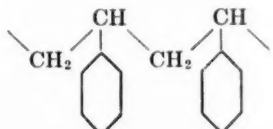
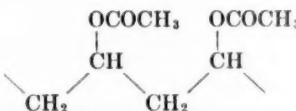
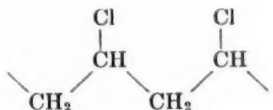
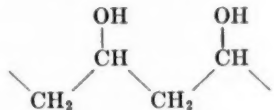
given by us previously for fractionated cellulose acetate¹⁵, polybutadiene¹⁷, and depolymerized gelatin¹⁸.

This lack of correlation results from the general concept of the macromolecular lattices of polymers, since the thermal fluctuations of the individual links play a more important role than the vibration of the entire macromolecule.

(2) *The form of the principal valence chain.*—The order of disposition of the atoms of carbon defines the form of the principal valence chain. This order has a substantial influence on the permeability of the polymer. An example of this effect is given by the difference in the permeabilities of rubber and gutta-percha to gases (see Table 2 and also Sager¹⁹). This difference is found despite

TABLE 3

THE INFLUENCE OF SIDE GROUPS ATTACHED TO THE PRINCIPAL VALENCE CHAIN ON THE PERMEABILITY, DIFFUSION, AND SORPTION OF HYDROGEN OF A SERIES OF POLYMERIZED OLEFINS

Polymer investigated	Structural Unit	$P \times 10^3$	$D \times 10^3$	$S \times 10^3$
Polyethylene		3.91	2.08	1.88
Polyisobutylene		5.02	2.42	2.07
Polystyrene		11.30	4.62	2.44
Polyvinyl acetate		7.47	3.66	2.04
Polyvinyl chloride		1.48	2.71	0.54
Polyvinyl alcohol		0.005	—	—

the fact that the two polymers have identical chemical constitutions. It has been found by Meyer and Mark²⁰ that rubber and gutta-percha are *cis*- and *trans*-isomers. The higher permeability values of rubber probably result from the increase in curvature in its macromolecules, leading to increasing size of the polymer. The low permeability of polychloroprene (Table 2) is probably due

TABLE 4

THE ACTIVATION ENERGY OF PERMEABILITY TO HYDROGEN OF VARIOUS POLYMERS

Polymer	$P \times 10^3$	Activation energy of permeability, in cal. per mol
Natural rubber	30.08	6400
Polybutadiene	34.06	6600
Polychloroprene	7.15	8160
Nitrocellulose	2.30	8280
Gelatin	0.20	7680
Hydrated cellulose (regenerated cellulose)	0.03	8270

in part to the presence of polar chlorine atoms as well as to the *trans*-form of the main valence chain, which is analogous in form to that of gutta-percha²¹.

(3) *The dimensions of side groups.*—The dimensions and form of the side groups of the macromolecule also have an important influence on the permeability to gases. As a first approximation, an increase in the dimensions of side groups causes an increase in permeability corresponding to the decrease in the interaction of the principal valence chains with one another (compare polyethylene and polyisobutylene, Table 3).

The higher permeability of films of polybutadiene (Table 2) possibly results in part from the branching structure of these macromolecules, which causes a decrease in the interaction of the main chains with each other.

(4) *The character of the intermolecular bonds.*—With regard to the question of structures, as determined by the interfaces of macromolecules, it can be seen that, in the ordinary course of events, an increase in the energy of intermolecular bonds accompanies a decrease in the permeability, due to simultaneous decreases in the coefficients of diffusion and sorption of hydrogen by polymers. Polymers in which the interaction of the molecules is due principally to dispersion forces (rubber, polystyrene, polybutadiene) have the greatest permeability. The lowest permeability is ordinarily observed where readily ionizable hydrogen or covalent bonds are present in the polymers. For example, it is well known that polymers having a closed or cyclic structure formed by covalent bonds have very low permeabilities, as shown by literature data on the permeability to hydrogen of bakelite²², ebonite²², Thiokol,²³ and certain resins¹⁷. Strong bonds between the chains lead to a decrease in the probability of the formation of "holes" and, therefore, to a reduction in the permeability of polymers. Corresponding to this is the observation that the introduction into the macromolecules of the polar groups OH, NH₂, COOH²⁴, or otherwise increasing the hydrophilic nature²⁵, causes a reduction in the permeability of the polymer. In particular, insignificant gas permeabilities are observed with polymers containing large numbers of polar groups, *e.g.*, polyvinyl alcohol (Table 2), hydrated (regenerated) cellulose²⁶, and proteins²⁷. It is presumed that, because of the polar groups, the macromolecules are in these cases oriented, with the formation of layered or diffuse structures²⁸.

The permeability to hydrogen of similar kinds of structures with high values for the energy of intermolecular binding might be considered to be high because of the greater activation energy, but this is not confirmed experimentally (Table 4). This lack of confirmation may be explained by means of the treatment advanced by Mark²⁹ dealing with the energy of bonds in a cellulose lattice. The energies are of the order of 50,000 cal. per mol for the covalent bonds along the axis of the chain, 15,000 cal. per mol for the hydrogen bonds between neighboring chains, and 8000 cal. per mol for van der Waals' forces.

Analogous results are obtained with proteins, which contain hydrogen, ionic, and covalent bonds and van der Waals' forces connecting separate parts of the side chains. It can be assumed that the penetrating molecules of gas proceed only by the action of van der Waals' forces, as a result of which these forces govern the identity of the activation energy of permeability of polar and nonpolar polymers. Low permeability of polar polymers in this event is obviously due to the limited number of possible paths for penetration of the hydrogen molecules.

SUMMARY

1. The permeability to gas of high molecular-weight polymers is closely connected with the character of the interaction between separate links of adjacent macromolecules, which is governed by the form of the chain and the energy of the intermolecular bonds.

2. The magnitude of permeability increases with increases in the curvature of the principal-valence chains and in the dimensions of the side groups, decreases with increase in the energy of the intermolecular bonds, and is independent of the length of the main valence chains.

3. A comparison of the values of the activation energies and gas permeabilities of a series of polymers makes reasonable the assumption that the principal paths for the penetration of hydrogen molecules lie along the interface between the nonpolar groups of the macromolecular chains.

REFERENCES

- ¹ Graham, *Phil. Mag.* **32**, 401 (1866).
- ² Wroblewski, *Wied. Ann.* **8** (1879).
- ³ Venable and Fuwa, *Ind. Eng. Chem.* **14**, 139 (1922).
- ⁴ Kayser, *Wied. Ann.* **43**, 544 (1891).
- ⁵ Stefan, *Wien. Ber.* **77**, 371 (1878).
- ⁶ Edwards and Pickering, *Bur. Standards Sci. Papers* **16**, 327 (1920).
- ⁷ In the original text, the author says that "this rate does not become constant." However, all other work on this subject, as well as the sense of what the author has just said, shows that the rate must become constant, particularly since the author applies Fick's law to the third period, and Fick's law applies only to a steady state. Although the statement in the original text is in the negative, this is probably an unintended error.
- ⁸ Daynes, *Proc. Roy. Soc.* **97A**, 286 (1920).
- ⁹ De Boer and Fast, *Rec. trav. chim.* **57**, 317 (1938).
- ¹⁰ Sager and Sucher, *J. Research Natl. Bur. Standards* **22**, 71 (1939); *RUBBER CHEM. TECH.* **12**, 875 (1939); Sager, *J. Research Natl. Bur. Standards* **25**, 309 (1940); *RUBBER CHEM. TECH.* **14**, 444 (1941).
- ¹¹ Barrer, *Nature* **140**, 106 (1937); *RUBBER CHEM. TECH.* **10**, 673 (1937); *Trans. Faraday Soc.* **35**, 628 (1939); **36**, 644 (1940).
- ¹² Barrer, *J. Chem. Soc.* **1934**, 378.
- ¹³ Barrer, *Trans. Faraday Soc.* **35**, 644 (1939).
- ¹⁴ Daynes, *Proc. Roy. Soc.* **97A**, 273 (1920); "Gas Analysis by Measurement of Thermal Conductivity," **1935**.
- ¹⁵ Reitlinger and Panyanina, *J. Applied Chem. U.S.S.R.* **12**, 886 (1939).
- ¹⁶ Sager, *Ind. Eng. Chem. Anal. Ed.* **9**, 156 (1937); *RUBBER CHEM. TECH.* **10**, 639 (1937).
- ¹⁷ Reitlinger and Letina, Report Ts. A.G.I. (1940).
- ¹⁸ Reitlinger, Report of Conference on Protein Problems (1940).
- ¹⁹ Sager, *J. Research Natl. Bur. Standards* **25**, 309 (1940); *RUBBER CHEM. TECH.* **14**, 444 (1941).
- ²⁰ Meyer and Mark, "The Structure of High Polymers."
- ²¹ Carothers, Collins and Kirby, *J. Am. Chem. Soc.* **55**, 789 (1933).
- ²² Barrer, *Trans. Faraday Soc.* **36**, 644 (1940).
- ²³ Sager, *India Rubber World* **94**, 31 (1936); *J. Research Natl. Bur. Standards* **19**, 181 (1937).
- ²⁴ Sager, *J. Research Natl. Bur. Standards* **13**, 879 (1934).
- ²⁵ Drinberg, *J. Phys. Chem. U.S.S.R.* **6**, 870 (1935).
- ²⁶ Trillat and Matricon, *J. chim. phys.* **32**, 101 (1935); De Boer and Fast, *Rec. trav. chim.* **57**, 317 (1938).
- ²⁷ Kanata, *Bull. Chem. Soc. Japan* **3**, 183 (1928); Reitlinger, Report of Conference on Protein Problems (1940).
- ²⁸ Sokolov, *Compt. rend. acad. sci. U.S.S.R.* **6**, 1487 (1937).
- ²⁹ Mark, *Chem. Rev.* **20**, 169 (1940).

A STUDY OF RUBBER-SULFUR MIXTURES BY RADIOMICROGRAPHY *

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It is a recognized fact that the size of sulfur particles and their state of dispersion in a mass of rubber play an important role in the vulcanization process. In the work described in the present paper, an attempt was made to develop a simple method by which the incorporation of sulfur into rubber could be followed and controlled. As a means to this end, the method of transmission radiomicrography already described by the author¹ was employed.

Samples of rubber, previously mixed with various percentages of sulfur, were placed between two thin sheets of cellophane 0.06 mm. thick, and pressed out at a temperature of 50°-60° C until the total thickness of the samples (rubber + cellophane) was 0.18 mm. The films prepared in this way were placed in a photographic plate holder, with care to obtain perfect adhesion to the special Lippmann film used in this technique.

The system was then exposed to radiation from a sealed tube with very sharp focus and with a copper anticathode, specially constructed to obtain this effect, and functioning under 8 kilovolts. Under these conditions the K rays of copper are not excited, and only radiation of the order of 2 A.U. acts on the system. The distance of the samples from the source of light was several centimeters; the time of exposure was 2 to 3 minutes. The photographic negatives obtained were subsequently enlarged several tenfold and in some cases several hundredfold.

The samples which were examined² included rubber-sulfur mixtures containing 1, 5, 10 and 32 per cent, respectively, of sulfur.

The first tests were carried out on the mixtures before they had been vulcanized. In the unvulcanized state the particles of sulfur were very clearly defined because of considerable absorption of the x-rays. By examination of the photographic negatives after enlargement, it was possible to determine the dispersion of the sulfur throughout the rubber, the uniformity of this dispersion, and the dimensions of the sulfur particles. It was possible also to construct a distribution curve, and to follow the influence of the time of mixing, both on the shape of the particles and their distribution.

The same samples were examined after they had been vulcanized for various times at 143° C. In this way it was possible to determine both the effects of the sulfur content and of the time of vulcanization.

INFLUENCE OF THE SULFUR CONTENT

Although, as mentioned above, the sulfur appeared very clearly before vulcanization, it was no longer identifiable after vulcanization. The radiographs of the samples vulcanized for 6 hours all showed a uniform gray color, with no visible spots due to sulfur, which was then dispersed homogeneously in the elastic mass in the form of combined sulfur, i.e., atoms of sulfur forming

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bridges between the hydrocarbon macromolecules. No trace of free sulfur could be detected, and therefore it could only be concluded that, after this long time of vulcanization at the particular temperature, practically all the sulfur had combined.

INFLUENCE OF THE TIME OF VULCANIZATION

To follow the progressive combination of sulfur with rubber, samples containing originally 32 per cent of sulfur were vulcanized for $\frac{1}{4}$ hour, $\frac{1}{2}$ hour, 1 hour, 3 hours and 6 hours at 143°C and examined as before. By means of radiographs it was possible to follow the progress of vulcanization in a particularly clear way.

In the sample which had been vulcanized for $\frac{1}{4}$ hour the greater part of the free sulfur appeared in the form of large flat droplets of elliptical shape, the formation of which is easily explained by the fact that sulfur fuses below the temperature of vulcanization (143°C). A comparison of the photographic negative of this sample with that of the unvulcanized control sample was particularly instructive in this respect.

Similar results were obtained with the sample which had been vulcanized for $\frac{1}{2}$ hour, except that there was already a diminution in the number of droplets, indicating further combination of sulfur with rubber. After vulcanization for 1 hour, the droplets of sulfur disappeared completely, but a bloom of crystalline character became visible. This crystalline bloom was still visible, but to a lesser degree, after vulcanization for 3 hours, but after the longest period of vulcanization it disappeared completely. It is attributable to free sulfur which exudes from the rubber and recrystallizes at the surrounding temperature. It may be asked why the free sulfur present as droplets does not have this same peculiar appearance. This question merits special study, for it is probable that only under special physical conditions is sulfur capable of recrystallizing in the form of a surface bloom.

The method described in the present work is applicable to the study of the influence of accelerators and the temperature of vulcanization, as well as to the control of the uniformity of dispersion of fillers. It has already been applied successfully to the incorporation of pigments in paints and varnishes.

REFERENCES

- Trillat, *Rev. scientifique* 4, 212 (1940); *Science et ind. photographie* 2, 1 (1942).
The samples were prepared by the Institut Français du Caoutchouc (French Rubber Institute).

RUBBER PHOTOGELLING AGENTS. II *

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Although certain aromatic amines and phenolic derivatives have long been used with success as "antioxidants" for the preservation of vulcanized rubber, very little is known respecting their protective action for unvulcanized rubber exposed to light. Blake and Bruce¹ showed that commercial antioxidants such as phenyl- β -naphthylamine promote the development of a tacky surface on unvulcanized rubber, while simpler substances, including sulfur, benzidine and hydroquinone, were able to hinder it. Later² they followed up this qualitative work with determinations of the oxygen absorbed by rubber, exposed to light, into which small quantities of various reagents had been milled. The simpler substances cited reduced the rate of oxygen absorption, whereas 0.5 per cent of phenyl- β -naphthylamine enhanced it. This effect was reversed by increasing the amount from 1 to 4 per cent. This reversal is significant, as will be shown later. Other antioxidants reduced the oxygen uptake, but it is clear that a definite conclusion cannot be reached without a range of values for each substance. Stevens and Gaunt³ exposed latex-treated cloth to ultraviolet light, and determined the acetone-soluble substances as a measure of oxidation. Here again the simpler substances were the most effective, as indicated by restriction of the amount of acetone extract. Some of these substances were vulcanizing agents, and it has been suggested that their protective action resulted from surface vulcanization⁴. Doubtless this is the case with sulfur, but it does not apply to the majority of the agents discussed in this paper.

Incipient vulcanization (cross-bonding) is readily detected by the gelation of a rubber sol protected from air and exposed to light. Consequently it was thought that some information might be obtained as to the nature of the protection afforded, or the reverse, by a series of exposures of rubber sols containing various proportions of reagent, both anti- and proöxygens, due regard being paid to the absence of oxygen (air) in the tubes or the presence of limited and measured quantities.

Experimental.—The general procedure was the same as detailed in the previous paper⁵. The solvents were either benzene or cyclohexane. The rubber mostly used was a well-milled pale crepe, the same sample throughout, but in some cases it was replaced by a diffusion rubber. The latter gells faster, and a 0.1 per cent solution can take the place of 0.5 per cent solution of milled rubber. Any complication arising from the presence of a protein network was thus avoided, as in one case it is eliminated and in the other broken down. Although it is not possible to state the exact time required to produce a gel, the gradual nature of the change from viscous fluid to firm gel can be followed. The stages reached by different tubes at the same time are recorded and a close comparison is maintained so that there can be no doubt as to the order of gelling and approximate time taken. The reagents employed fall into five classes.

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 64, No. 11, pages 312-315, November 1945. Part I appeared in the *Journal of the Society of Chemical Industry*, Vol. 64.

- (1) Commercial antioxidants, aminic and phenolic.
- (2) Simpler substances, also both aminic and phenolic.
- (3) Accelerators possessing antioxygenic properties.
- (4) Proöxygens, such as copper oleate and cobalt linoleate.
- (5) Vulcanizing agents, including sulfur, oxygen and trinitrophenol.

Insolation in the Absence of Air.—By allowing the rubber to swell and partly disperse in the solvent while under reduced pressure overnight and boiling off again before sealing, the oxygen dissolved in the rubber is removed, as well as that in the solvent. In this way it was found possible to remove the air so completely that, in the absence of any activator, gelling did not take place, however long the exposure. Therefore any gelling in the presence of agents can confidently be ascribed to those agents. The following is a list of the most reactive, with the time taken to form a firm gel not displaced by shaking the tube. All are 5 per cent sols of milled crepe.

All the above antioxygens have gel-promoting properties. A number of tubes would be necessary to ascertain the optimum proportions in each case, but of the first three, 0.1 per cent is more effective than 1.0 per cent. It also appears that they are much less active as gelling agents than ketones or quinones.

TABLE I
MAXIMUM RATE OF GELLING AND OPTIMUM AMOUNT OF REAGENT

Reagent	Percentage on rubber	Time to gel (hours)
Phenyl- β -naphthylamine	0.1	14
Triphenylhydroquinoline	0.1	14
Aldol- α -naphthylamine	0.1	24
Triphenylhydroquinoline	1.0	28
<i>p</i> -Phenylenediamine	0.2	43
Di- β -naphthyl- <i>p</i> -phenylenediamine	1.0	45
Nonox-S	0.4	47
Aniline	2.0	65
Benzidine	2.0	69
<i>p</i> -Phenylenediamine	2.0	100+

Insolation in the Presence of Air.—Gelling is promoted by the presence of a little air equivalent to 0.2 per cent or thereabouts of oxygen on the rubber, and is further promoted by the addition of small quantities of the more efficient of the above-mentioned antioxygens. Thus 0.1 per cent of phenyl- β -naphthylamine in a 1 per cent sol of diffusion rubber gave a firm gel in 6 hours. In the absence of air a firm gel could not be obtained at this dilution.

Several series of tests were made with 0.5 per cent milled rubber sols enclosing small quantities of air equivalent to 0.2–0.3 per cent oxygen on the rubber. The times taken to gel are plotted as curves in Figures 1 and 2. Smooth curves could not be drawn for the antioxygens shown in Figure 1 or for *p*-phenylenediamine in Figure 2. These show sharp breaks. The other curves can be drawn smoothly but show sharp bends. The breaks or bends all lie in the region of low proportions, not exceeding 0.5 per cent, often as low as 0.1 per cent on the rubber. That is to say, all the reagents promote gelling in small proportions, but rather suddenly reverse this property when the proportions are increased. The figures record the times taken to form firm gels (a few determinations lie outside the graphs), but frequently the larger proportions do not completely inhibit gelling and there is a gradual recession from a firm gel to a weak one

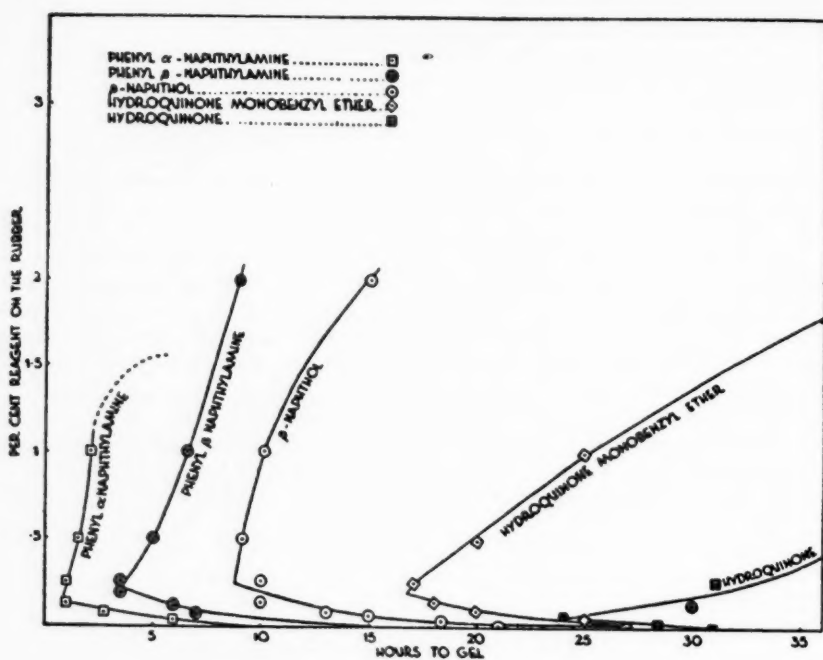


Fig. 1

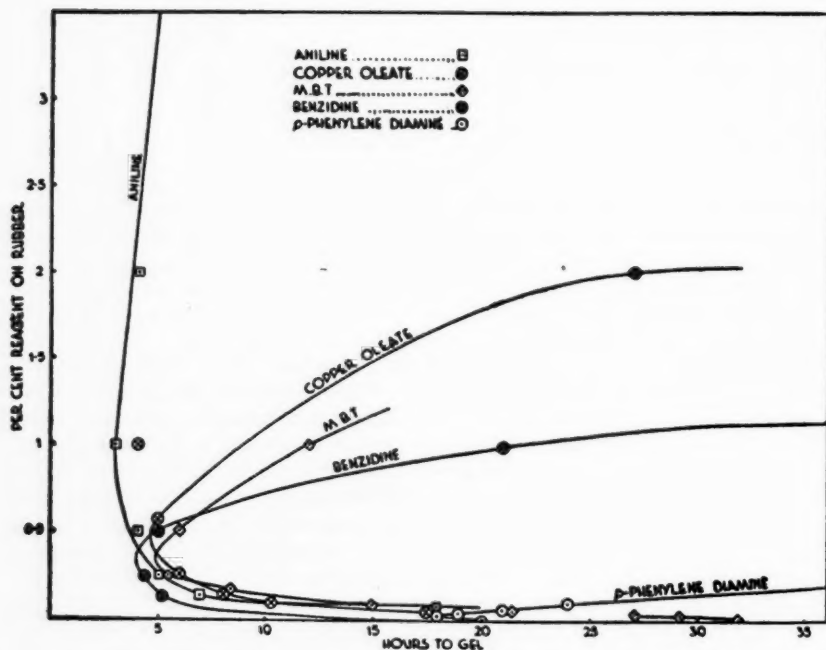


Fig. 2

and then to partial gelling or mere increase in viscosity. Aniline is the only reagent which failed to prevent gelling entirely (maximum proportion used was 4 per cent). Hydroquinone and *p*-phenylenediamine show reversion at very low concentrations. Most of the reagents in the list are antioxygens, but copper oleate behaves in the same manner as the antioxygens, as also the accelerator mercaptobenzothiazole. Others, including cobalt linoleate, not shown in the graphs are given in the list below.

Cobalt linoleate is a weak promoter. Whereas 1 per cent copper oleate reduced the time of gelling from 30 hours to 4 hours, the linoleate reduced it to 19 hours.

Vulcanizing Agents.—The effect of sulfur as a gelling agent was discussed in the previous paper, and it was shown that 0.5 per cent was about the minimum necessary to form a firm gel. No advantage was obtained by adding more than 1 or 2 per cent, as with larger quantities the rate of gelling tends to slow down. Whether this is due to the opacity of the undissolved sulfur or directly

TABLE II
MAXIMUM EFFECTIVE PROPORTIONS OF ANTI- AND PROÖXYGENS AS
GELLING AGENTS

Reagent	Percentage on rubber
<i>p</i> -Phenylenediamine	0.0125
Hydroquinone	0.0625
Phenyl- α -naphthylamine	0.125
Phenyl- β -naphthylamine	0.25
Hydroquinone monobenzyl ether	0.25
Benzidine	0.25
β -Naphthol	0.5
Mercaptobenzimidazole	0.5
Mercaptobenzothiazole	1.0
Aniline	1.0
Resorcinol	1.0
Copper oleate	1.0
Cobalt linoleate	1.0

to the excess of sulfur it is not possible to say. Benzoyl peroxide is also a gelling agent in small proportions. Exposures were also made with trinitrotoluene as an example of another type of vulcanizing agent, both with and without lead peroxide and in the absence and presence of air. Very slight gelling activity was observed with proportions under 0.5 per cent. Larger quantities retarded. The contents of the tubes with more than 0.5 per cent were still mobile after 70 hours' exposure.

Varying Proportions of Oxygen.—In the previous paper it was shown that very small proportions of oxygen strongly promote gelling. In the presence of a powerful activator such as anthraquinone and in quantities such that gelling is a matter of a few minutes exposure, the presence of oxygen has little or no influence; in fact gelling will take place in an open tube, although the surface of the gel first formed is gradually eroded, and liquifies from the surface downwards. With mild activators such as the substances under consideration and with which there is plenty of time for the oxygen to diffuse into the sol from the air above, increasing proportions of air result in delayed gelling, much as happens in the absence of an activator. The following tables illustrate this point.

TABLE III
VARIATION IN VOLUMES OF AIR SPACE AND PROPORTIONS OF ANTIOXIDANT

Percentage of β -naphthol on rubber	Percentage of oxygen on rubber	Hours to gel
1.00	0.07	10
1.00	0.24	13
0.25	0.11	10
0.25	0.27	14
0.063	0.15	13
0.063	0.23	15
0.016	0.12	18
0.016	0.28	25
nil	0.13	27

TABLE IV
VARIATION IN VOLUME OF AIR SPACE WITH 1% COPPER OLEATE
AS PROÖXYGEN ON THE RUBBER

Percentage of oxygen on rubber	Hours to gel
0.02	2.5
0.13	4
0.38	7
0.54	9
nil	20

Similar results were obtained with other reagents. If, however, the amount of reagent is only just sufficient to prevent the formation of a firm gel, extra air may in time enable a firm gel to be obtained. Thus with 1 per cent of hydroquinone and a series containing air equivalent to 0.1 to 1.0 per cent oxygen, that with least air began to show signs of gelling after about 30 hours and had formed a weak gel in 40 hours, but did not get beyond this stage. The tubes with 0.7 to 1.0 per cent oxygen were still quite fluid after 40 hours, but all had set to firm gels after 60 hours' exposure.

Le Bras⁶ has recently drawn a distinction between antioxidants which inhibit the combination of oxygen with rubber and therefore decrease oxygen absorption, and deactivating antioxidants, which deactivate the peroxides transforming them into oxides. It is difficult to understand how this can render the peroxides harmless, since this transformation to oxides is the process by which oxidative chain-splitting is effected. Le Bras instances mercaptobenzimidazole as an antioxidant of the latter type. Through the kindness of W. J. S. Naunton, the writer was enabled to make a gelling test with this substance and to compare its action with mercaptobenzothiazole and other antioxidants. It was found to behave in the same manner as the others and to closely resemble mercaptobenzothiazole in activity. Nothing is known regarding the fate of antioxygens in raw rubber, and it seems useless to speculate further until work in this direction is more advanced.

DISCUSSION

From the foregoing it is clear that the agents when used in small proportions act as mild activators but this effect is suddenly reversed at some stage, larger proportions inhibiting gelation. Also that proöxygens and antioxygens act in a similar and not in an opposite manner, as would be expected. Gelation takes

place both in the absence and presence of air in limited proportions. The true activators such as ketones, aldehydes and quinones differ from the above in that they act most efficiently in the absence of oxygen and the presence of air always tends to delay gelation. They are also as a class far more efficient.

Any substance which induces gelling has a twofold action: (1) by promoting cross-linking, which may or may not involve the inclusion of oxygen or other element in the link, and (2) by promoting or retarding oxidative degradation in the form of chain splitting or as rupture of the cross-linkages first formed. There is no obvious reason why either anti- or proöxygens should possess cross-bonding activity. It seems, however, that they must possess such activity, otherwise they would not promote gelation. Further, the reversion or loss of activity which occurs when they are present in larger proportions must also result from their peculiar reactivity. It would seem that two reactions are in progress, the nature of which is at present unknown. They are, however, quite unconnected with the complementary oxidizing or reducing properties of the agents, since both anti- and proöxygenic substances bring about the same change (gelation) or the reverse.

Under (2), oxidative degradation, the agent functions either as a promoter or retarder, but it is important to bear in mind that no elucidation of the reactions involved, whether oxidizing or reducing, can explain the cross-linking properties which can proceed without the agency of oxygen or in the presence of very minute quantities. Ordinarily, antioxygens should promote gelling by restricting oxidative chain scission and proöxygens the reverse. There is, however, no indication from the experimental data that they do in fact exert such opposite actions, and therefore these reactions do not play any very important part in controlling gelation. In the presence of air (oxygen) gelation is usually delayed as in the absence of any agent, but on the other hand, the oxygen may play the part of an additional catalyst or activator and eventually bring about the gelling of a sol, which in the absence of oxygen or when present in smaller proportions does not take place or only imperfectly.

In general, the substances reported on have little influence on the oxidative processes, and consequently these are not the determining factor in causing gelation. This must be looked for under process (1), which takes place either independently of oxygen or requires so little that in such cases oxidative scission hardly comes into play.

SUMMARY

A previous paper detailed the evaluation of oxygen and other photogelling agents under insolation. This paper deals similarly with various pro- and antioxygens, and it is shown that in small proportions all these act as mild photogelling agents, the effect being rather abruptly reversed when the proportion exceeds the optimum. The relevant factors are discussed.

REFERENCES

- ¹ Blake and Bruce, *Proc. Rubber Tech. Conf. London*, 1938, p. 736.
- ² Blake and Bruce, *Ind. Eng. Chem.* **33**, 1198 (1941).
- ³ Stevens and Gaunt, *Proc. Rubber Tech. Conf. London*, 1938, p. 686.
- ⁴ See, for example, Naunton, *Proc. Rubber Tech. Conf. London*, 1938, p. 746.
- ⁵ Stevens, *J. Soc. Chem. Ind.* **64**, 135 (1945).
- ⁶ Le Bras, *Compt. rend.* **217**, 297 (1943).

THE HARDENING OF CRUDE RUBBER *

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Everyone who has handled crude rubber or has seen this material in process is familiar with the fact that bales of rubber, whether crepe or smoked sheet, become hard when they remain exposed to temperatures below about 10° C. The rubber is said to be frozen. When in this state bales of rubber are very difficult to cut, and it is usually necessary to store them in a hot room for a long time in order to thaw them. Even when presses sufficiently powerful to cut such hard bales are available, it is still necessary to heat the cut pieces before they can be put on a mill. This extra handling and expense are only an inconvenience in rubber manufacture.

This freezing phenomenon would seem to be relatively simple, and as is shown clearly by x-ray diagrams, would seem to be the result of "crystallization" of the rubber. Actually, however, the phenomenon is unquestionably more complex, since these changes do not take place at any fixed temperature. Moreover, certain observations which the present author has made show that the phenomenon is influenced to a considerable degree by the operating conditions.

Suppose, for example, that a sheet of crude unmilled rubber is rolled up while the sheet is held under slight tension during the rolling. The rubber in the roll then remains under tension. Let this roll of rubber be pressed out cold¹ in a suitable press to a flat sheet. It can be shown that the sheet thus obtained freezes much more readily than the original rubber and that it thaws much less readily.

It would appear that what has been accomplished in this experiment is nothing more or less than some sort of racking. Without going into too detailed a discussion, it would seem reasonable to believe, from what is known about racking, that the molecules are oriented in some way², and consequently that orientation takes place also in the experiment described above.

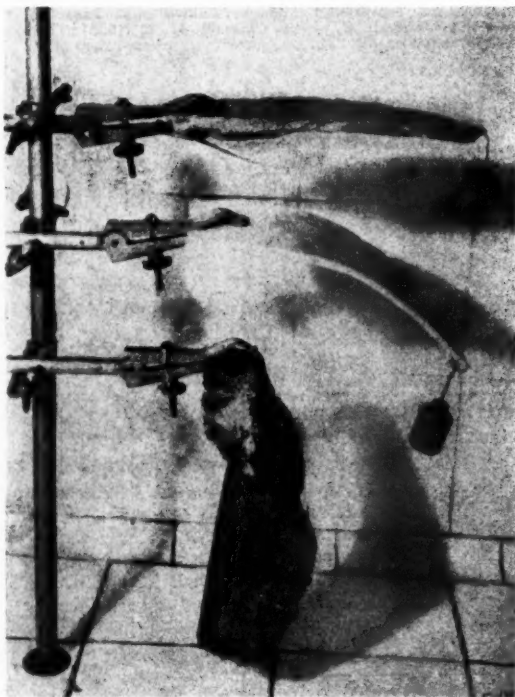
If a more highly oriented state of the rubber molecules facilitates freezing, it might be expected that freezing would be obstructed by a disordered state of the molecules, i.e., by the elimination of all internal stresses. To prove or disprove this, the experiment was repeated, but this time the sheet was pressed out at 80° C for the same length of time (2 hours).

Let us now compare the results obtained when the original rubber and the two samples which had been rolled up under tension and pressed out as described above were kept at 0° C for 24 hours. The accompanying photograph shows the very marked difference in behavior of the three samples. The roll which was pressed out at room temperature (top sample in photograph) became as hard as wood, and remained absolutely rigid even when a weight of 100 grams was suspended on its free end. The original crepe, which had not been

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milled (middle sample in the photograph) also froze, but it was much less stiff than the top sample. The roll which had been pressed out at 80°C (bottom sample in photograph) remained soft and did not freeze at all.

These differences persisted even one year after the samples had been pressed out, in spite of their having been kept at room temperature ($18\text{--}25^{\circ}\text{C}$) throughout the year.



Appearance of the three samples after resting for 24 hours at 0°C .

It follows that, when crude rubber is pressed out while hot, its tendency to freeze is lessened. When it is considered how sheets of rubber are packed on the plantation, it is evident that the method is a definite contributing factor to the tendency of rubber to freeze. Actually the sheets of rubber are piled on one another and highly compressed in the cold state in powerful presses before being baled. It is quite possible that if this operation, instead of being done at room temperature, were to be carried out at 80°C , the blocks obtained would have a greater tendency to retain their original plasticity. Only by tests on the plantations would it be possible to verify this assumption. If it did turn out to be true, such a process of packaging would give in a very simple way a means of obtaining special grades of crude rubber which would be greatly valued by the rubber manufacturing industry because of the greater resistance of such rubber to freezing.

REFERENCES

¹ By cold is meant at ordinary temperatures.

² It is interesting to compare these phenomena with the studies of the magnetic anisotropy of rubber undertaken by Cotton-Feytis (*Compt. rend.* 214, 485, 996 (1942); 215, 299 (1942); *Rev. gén. caoutchouc* 19, 91 (1942). Particularly noteworthy are the phenomena observed with cylindrical test-specimens prepared by simple coagulation of latex in test tubes, and which were then either stretched or compressed. It was found that, in all cases, the direction in which the specimens were kept stretched tended to orient itself parallel to the lines of force when the samples were placed in the field of a small electromagnet, whereas the direction in which the specimens were kept compressed oriented itself perpendicular to these lines of force. This is new proof, furnished by measurements of magnetic anisotropy, that compressive forces in rubber involve orientation phenomena analogous to those which appear in the case of tensile stresses. It is known, in fact, that Thiessen and his collaborators have shown that compressed rubber crystallizes in the same way that stretched rubber does (cf. Thiessen and Wittstadt, *Z. physik. Chem. B*, 41, 33 (1938); Thiessen and Kirsch, *Naturwissenschaften* 26, 387 (1938)).

X-RAY INVESTIGATION OF THE CALENDER EFFECT IN RUBBER SHEETS *

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If masticated rubber is calendered by a three-roll calender, with the rolls at the same temperature, *e.g.*, 80° C, and the sheet is allowed to cool freely after calendering, the rubber sheet obtained has the same mechanical properties both in the transverse and longitudinal directions. If, on the other hand, calendering is carried out with a cold third roll, the sheet shows a large difference in mechanical properties in the two directions. This phenomenon is generally called the calender effect.

Rubber sheets, calendered with and without a calender effect¹ were submitted to x-ray investigation. Little work has so far been done on this subject; the work of de Visser² seems to be incomplete in this respect.

First latex crepe was masticated for 8 minutes at 55° C, after which it was calendered. The three calender rolls were heated by steam and all kept at a temperature of 80° C to obtain a rubber sheet without calender effect (sample A). Afterwards the temperature of the third roll was lowered at 20° C, the result of calendering being a sheet with strong calender effect (sample B). The mechanical properties of the sheets A and B are shown in the following table.

TABLE 1

	Mechanical properties of rubber sheets			
	Direction perpendicular to the axis of the calender rolls		Direction parallel to the axis of the calender rolls	
	Tensile strength (kg. per sq. cm.)	Elongation at break (percentage)	Tensile strength (kg. per sq. cm.)	Elongation at break (percentage)
A	7.0	620	5.3	940
B	14.3	120	3.7	870

A: sheet with a slight calender effect;

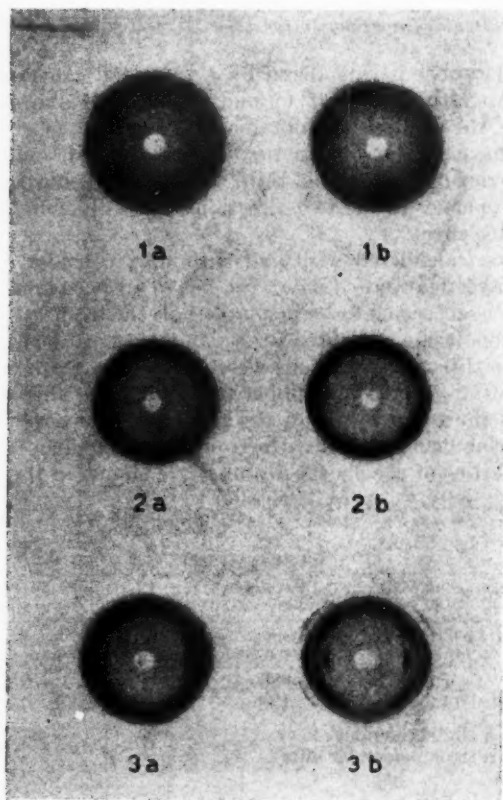
B: sheet with a strong calender effect.

From these figures it is obvious that sheet B shows a very strong calender effect; on the other hand A is not entirely free from this effect owing to experimental difficulties.

Two days after calendering, the x-ray diagrams reproduced in Figure 1a and b were obtained. No difference between the patterns can be seen, and traces of crystalline structure cannot be detected. This is at variance with the observations of de Visser, who found that a sheet with a strong calender effect always showed x-ray reflections, the cause of these reflections not being explained, however. As time went on, evidence of increasing crystallization appeared, preponderantly in sample B. This may be seen in Figure 2a and b, these diffraction patterns being taken five weeks after calendering. During

* Reprinted from the *Mededeelingen van de Rubber-Stichting*, No. 33, May 1942, 4 pages. This paper was published also in *Physica*, Vol. 9, 213 ff. (1942).

that time the rubber was kept at an average temperature of about 11° C. The direction of the *b*-axis of the crystallites is noteworthy, being approximately perpendicular to the roll axis. Accordingly the rubber chain molecules are drawn parallel by calendering, but not yet forced into a lattice. This state is fixed by a low temperature of the third roll, in accordance with the current view of the calender effect. Gradually the molecules "click" into a crystalline lattice, those of A however much slower than those of B; this seems



FIGS. 1-3.—X-Ray diagrams of rubber sheets with slight and with strong calender effect.
a, Diagrams of sheet with slight calender effect; b, Diagrams of sheet with strong calender effect.

acceptable in view of the higher orientation in the latter. The result of this process can be seen in Figure 3, which was taken three months after calendering. Further increase of the degree of crystallization seems unlikely, because keeping the rubber at -5° C during one week did not change the x-ray patterns. The oriented crystallization of the sample A, though far less than that of B, is probably due to the fact that sample A is not entirely free from calender effect.

Further possible research would be to carry out combined measurements on density and mechanical properties, in close connection with x-ray work.

SUMMARY

Rubber sheets were calendered with a slight and with a strong calender effect. The x-ray diagrams did not show any crystalline structure 2 days after calendering. Gradually x-ray reflections developed, the sheet with calender effect showing the reflections much quicker and stronger than the one with a slight calender effect.

ACKNOWLEDGMENT

We are grateful to Prof. Dr. H. B. Dorgelo for facilities rendered in the X-Ray Department of the Laboratorium voor Technische Physica, Delft.

REFERENCES

- ¹ Van Rossem, *Rubber Age* (London) 2, 376, 397 (1921); *India-Rubber J.* 62, 343 (1922).
² De Visser, "Het kalandereffect en het krimpeffect van ongevulkaniseerde rubber." Diss. Delft, 1925; translated in English: "The Calender Effect and the Shrinking Effect of Unvulcanized Rubber," Crosby Lockwood & Sons, London, 1926.

MECHANISM OF RUBBER CRACKING *

E. F. POWELL AND V. E. GOUGH

INTRODUCTION.—Rubber and rubberlike polymers, in common with other materials which deteriorate on exposure to oxidizing or similar agents, eventually crack under normal atmospheric service conditions. The present paper confines itself to the factors affecting the type and appearance of the cracking which eventually occurs when a surface film of a rubber object (particularly when stressed) hardens and deteriorates in strength from any cause whatsoever.

The importance of an understanding of the effects of exposure conditions on the character of the cracking produced cannot be too highly emphasized. This is so even if interest is confined solely to simple tests on new protective paints on an acceptance basis rather than research into surface deterioration. It is probable that many protective agencies have been accepted or rejected for extensive production tests because the initial laboratory tests have either not been representative of service or have been inadequate in scope. This still remains a major problem.

The theory presented here has gradually taken shape over a period of some ten years and appears to describe adequately the general findings on the whole gamut of cracking, *viz.*, fine check cracking and isolated deep cracks produced under service and laboratory conditions, the latter covering flexing, roof exposure, ozone and similar tests.

CHANGES OF PHYSICAL PROPERTIES OF AGED SURFACES.—Evidence of changes in the physical properties of the surface layers of rubber during exposure is perhaps not necessary, as it is well known that rubber loses strength and hardens on exposure. Figure 1 is, however, of interest in that it shows a comparison of the tensile strength and elongation when rubber compounds are shelf aged: (1) in a solid block from which 4 mm. test slabs are cut at intervals, and (2) as 4 mm. slabs. The curves based on tests on organic and inorganic accelerated compounds show that the changes in properties are mainly surface phenomena, and clearly the actual surface of the 4 mm. slabs alter much more than the recorded results.

STATISTICAL NATURE OF THE DISTRIBUTION OF THE CRACKS.—From the above it follows that the surface film of an aged rubber article has, when deformed so that the surface is in tension, a higher stress than the immediate layers below it due to the stiffening, and the surface layers have a considerably lower tensile strength to withstand this stress. As aging and stressing, or aging alone, continue, the tensile strength falls below the applied stress and the surface film breaks.

Now the tensile strength, even when the rubber is freshly moulded, is not a definite unique value, constant throughout even a small sample. It is distributed in the statistical sense. A range of tensile strengths can occur, and the relative probabilities of occurrence follow an ascertainable law¹. As is true of every other physical or chemical property, the resistance to surface

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 2, pages 102-113, August 1945.

changes due to exposure, and therefore the chance of a crack, is distributed in the manner of a probability. Figure 2 shows that the pitch or distance apart of adjacent cracks follows such a law. Figure 3 shows more data relating to crack depth at various times of outdoor flexing. Similar curves can be obtained from ozone or static tests.

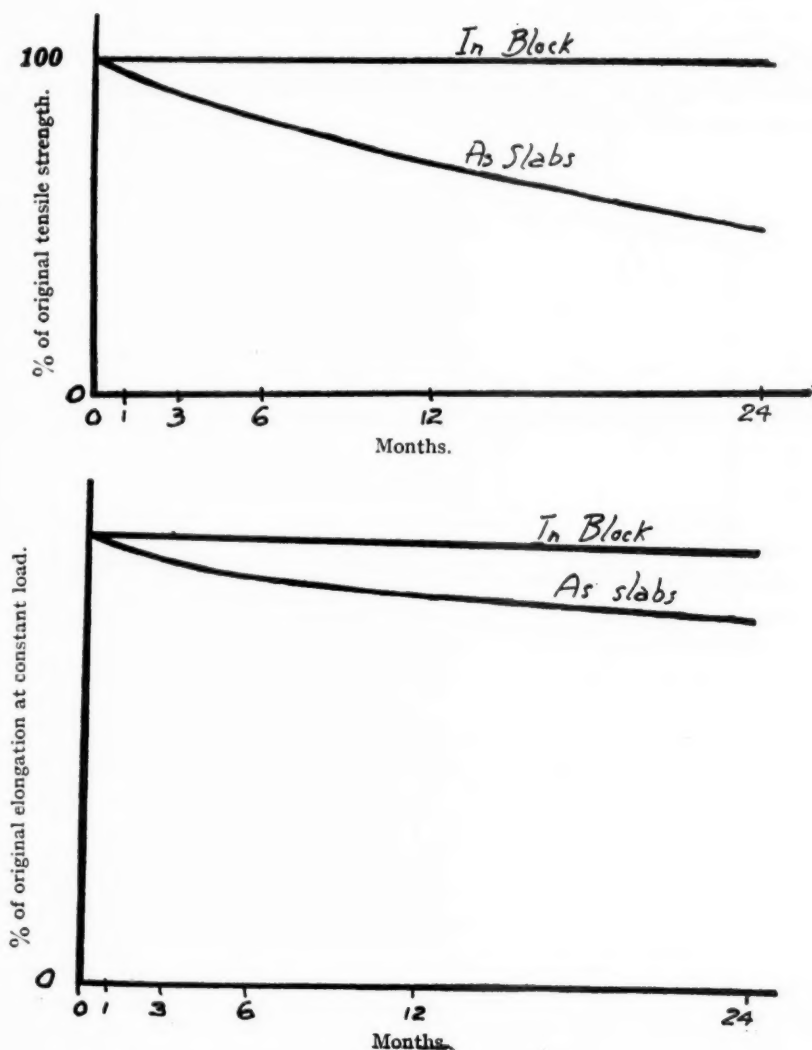


FIG. 1.—Changes of tensile properties when exposed in alternative forms.

ORIENTATION OF CRACKS.—The length of a crack is, as is well known, at right angles to the direction of the tensile stress causing the fracture. Figure 4a shows that the maximum stress around a circular hole is three times that

of the general tension in the plate, and is in the diameter normal to the applied tension.

The stress concentration is greater in the case of an elliptical hole with the major axis normal to the direction of pull (see Figure 4b). The ratio in which the stress is raised is even greater if the hole is a mere slit.

There is an important point in the case of holes inclined so that the major axis is not at right angles to the line of pull. The maximum stress is not at the smallest radius of curvature, but is approximately at the points where the tangents are parallel to the axis of pull (see Figure 4c). Hence even if a crack starts inclined to the usual direction, there is greatest tendency for the tear to continue along the usual direction.

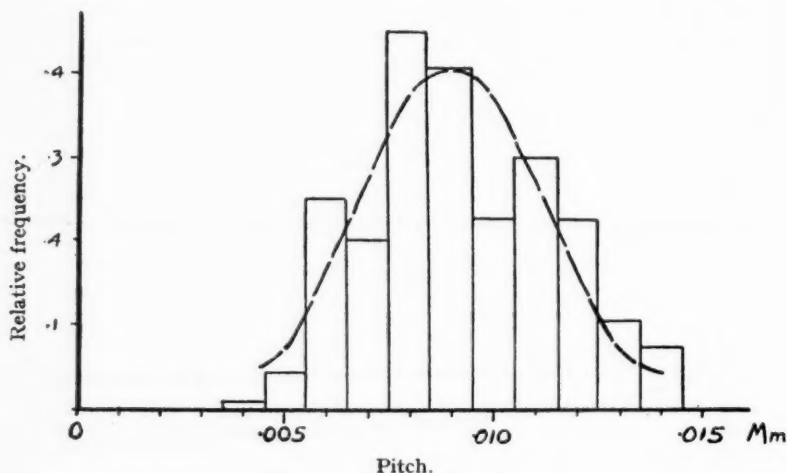


FIG. 2.—Distribution of pitch of cracks (sample flexed outdoors 12 hrs. 1000 cycles per min.).

Similar considerations of the stress concentrations at the bottom of grooves and slits in tension members or beams show that the tensile stress is a maximum at the bottom of groove or slit in such a position that a crack continues to grow in a direction normal to the rubber surface (Figure 4d).

RATE OF PROPAGATION OF EXISTING CRACKS.—The presence of the cracks already formed redistributes the stress in such a way that a crack propagates itself in depth into the bulk of the rubber, increases in length, and releases the surface stress locally. These three effects have a profound control over the nature of the cracking, and are as important as the probability of cracking.

Cracks deeper than their neighbors proceed rapidly into the bulk of the rubber because of the stress concentration at the root and the aging or deterioration continuing to a lower depth than the general depth below an intact surface.

The length and depth of cracks are roughly in unison, as would be expected from the fact that an increase in crack depth raises the local stress in the rubber at the ends of an existing crack. Figure 5 shows that the length and depth of large cracks are related.

The release of stress which accompanies the stress concentration at the ends and bottom of a crack is a local effect only, and the stress release due to a crack

does not extend beyond a distance of the same order as the length or depth of the crack.

This follows from St. Venant's principle (from the theory of elasticity), which can be stated in the form that the effect of any system of forces on a

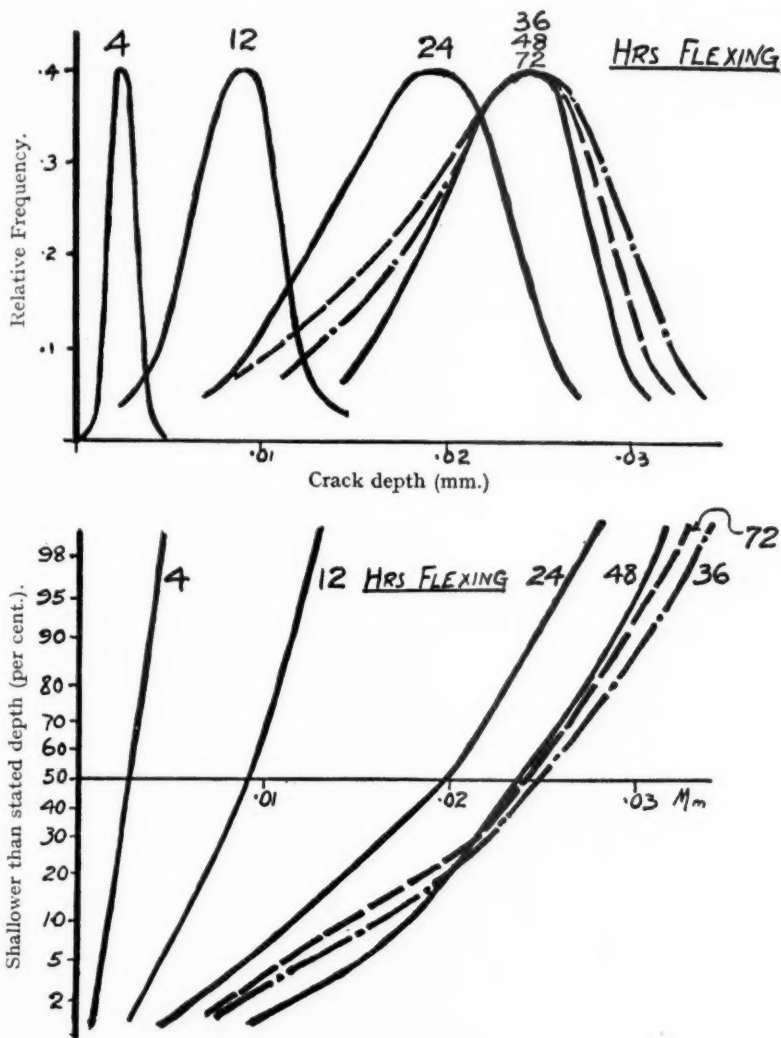


FIG. 3.—Distribution of crack depths.

body on the stresses and hence distortion in remote parts of the body, situated at a distance large compared with the dimensions of the area on which the forces operate, is indistinguishable from the effect caused by the resultant of that system of forces applied at the position it would occupy if it replaced that

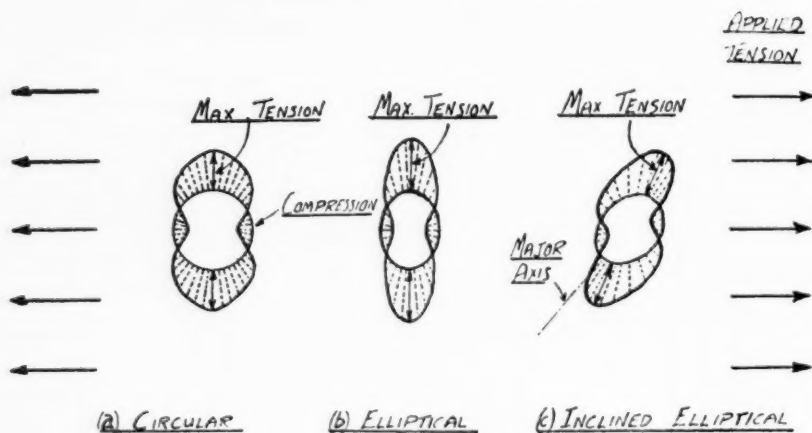


FIG. 4.—Stresses around edges of holes in a plate under tension.

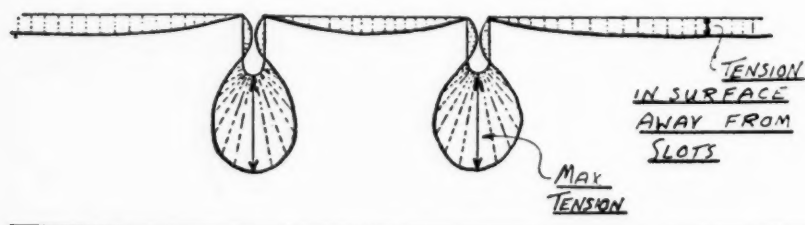


FIG. 4D.—Tension in surface of slots in a beam

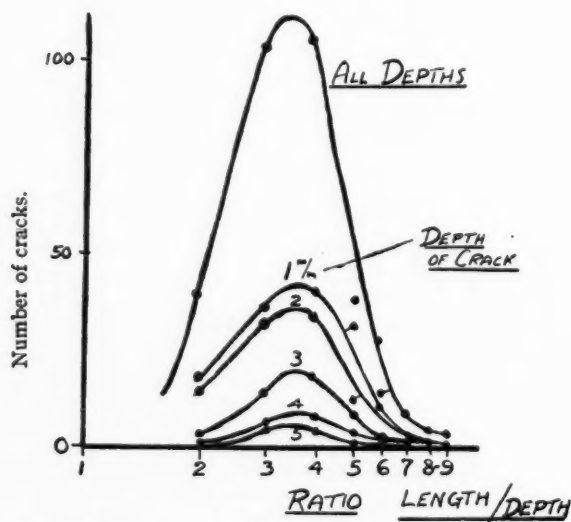


FIG. 5.—Distribution of ratio of length to depth of cracks (isolated deep cracks).

system. Hence the stress distribution in the major part of the surface is unaffected by a crack forming at a point but locally the surface stress is relieved.

The net effect is that shallow cracks closely adjacent to deeper ones do not continue to grow at the same rate, and so the range of depth gets greater as time increases. This is illustrated by Figure 6 showing the number of cracks of known depth at various total flexing times (same samples as Figure 3). The apparent number of cracks decreased with time because, as the deeper cracks developed with time, it was impossible to distinguish the finer cracks from surface roughness as insufficient surface stress could be applied to open up the finer cracks immediately adjacent to the deeper cracks.

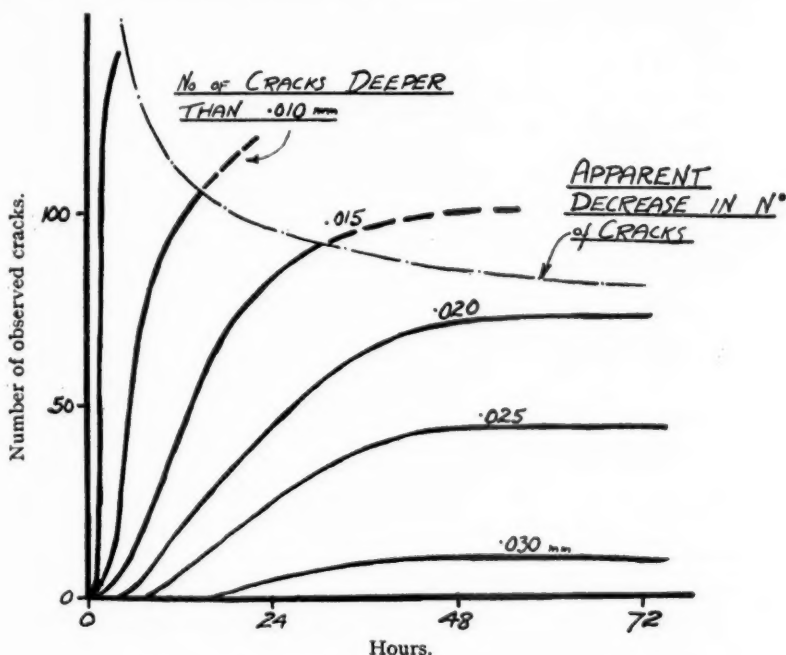


FIG. 6.—Number and depth of cracks after various times of flexing.

INFLUENCE OF PERCENTAGE STRETCH.—As already stated, the pitch and severity of the cracking depends on the number of cracks and the rate of development in depth. The percentage stretch has an influence on both these factors. The probability of cracking increases with applied stretch even if the rate of change of properties by exposure, *i.e.*, attack by ozone, is independent of stretch. This is because the stress due to the applied tension exceeds the tensile strength of the deteriorated surface at more places when the stretch (or stress) is high than when it is low. Conversely fewest cracks occur at the lowest stretches for the same reasons; that is, considerable reduction in surface strength is essential to form a crack at a low stretch, and the probability of such a big local drop is low and occurs only at a few points on the surface.

In the case of the low stretches, it also follows that cracks which do form progress very markedly, as the probability of relief by cracks close enough to

modify the stresses is low. The cracks already formed, which are few in number, therefore progress more rapidly into the bulk of the rubber than the considerably larger number on the highly stretched samples.

This rapid development in depth has a further secondary effect of reducing the available area for new cracks to form because, from St. Venants principle, it follows that the stress is released over a bigger area per crack. Ultimately, new cracks are prohibitively difficult to form because of this release of stress on the isolated lands between the adjacent cracks, with the consequence that serious deep cracks result from the necessarily increased stress concentrations at the bottom of the cracks.

It will be seen that this theory removes completely the necessity for the concept of a critical stretch, which has worried workers in this field for many years. A critical stretch (at which rate of attack by ozone or oxygen is a maximum) is extremely difficult to explain on a chemical or physical-chemical basis. The explanation is the simple one; it does not exist.

Somerfield² published comparative curves of loss of tensile strength in oven, ozone and oxygen aging, which show the enhanced deterioration at low stretches in ozone and oxygen. The authors' theory explains the shape of these curves, without assuming that the rate of chemical attack is affected by stretch at all.

In point of fact the theory indicates that the stretch which gives maximum deterioration may well depend on exposure conditions as well as on the compound or polymer employed.

CONSEQUENCES OF THE THEORY.—There are several important consequences of the ideas outlined above. The agreement between the experimental data and deductions from the theory form the justification of the theory.

Effects of Shading Samples in Exposure Tests.—Careful experimental work will reveal, contrary to popular belief, that samples exposed to direct sunlight do not always take up a worse appearance than similar samples exposed at the same time under the same conditions but shielded from the direct sunlight. The explanation is that the probability of crack formation is much greater in the case of the sample receiving the sun's rays, and large numbers of cracks are formed which fail to develop owing to stress release. After the same time of exposure the lower probability of attack, due to the shielding, results in fewer cracks, which, in the absence of stress release, becomes serious and the whole sample not only has a worse appearance but has lost more useful cross-section.

Protective Paints and Veneers.—It is often thought that, provided an anti-cracking paint has passed an arbitrary exposure test, its superiority under all conditions of exposure is established.

From the present theory, it follows that short-term tests, however made, stand a big risk of being misleading, due to the relative magnitudes of probability of cracking and rate of propagation not being typical of service conditions.

One or two conclusions can be drawn which would appear to be independent of such effects. The use of the normal type of protective film, while delaying the onset of cracking, ultimately results in cracks much deeper than those which occur in an unprotected surface at the same stretch, and exposed at the same time. This is amply confirmed by paint tests and work on synthetic rubber veneers (see Figure 7). When cracking does start, it is of a particularly serious type.

The whole value of many protective paints and applied synthetic veneers is the delay they cause in the onset of cracking. For such treatments to be

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fully effective the delay must equal the normal operational life of the rubber article. Any pinholes or weak spots in the applied film can constitute a serious menace.

In any case the application of a homogeneous layer of material of high resistance to cracking (though slightly pervious to ozone) over an object made of a material of poor cracking properties inevitably results in coarser cracking than the unprotected material. This is precisely because the filtering effect of the protective film reduces the probability of inception of cracks. Hence

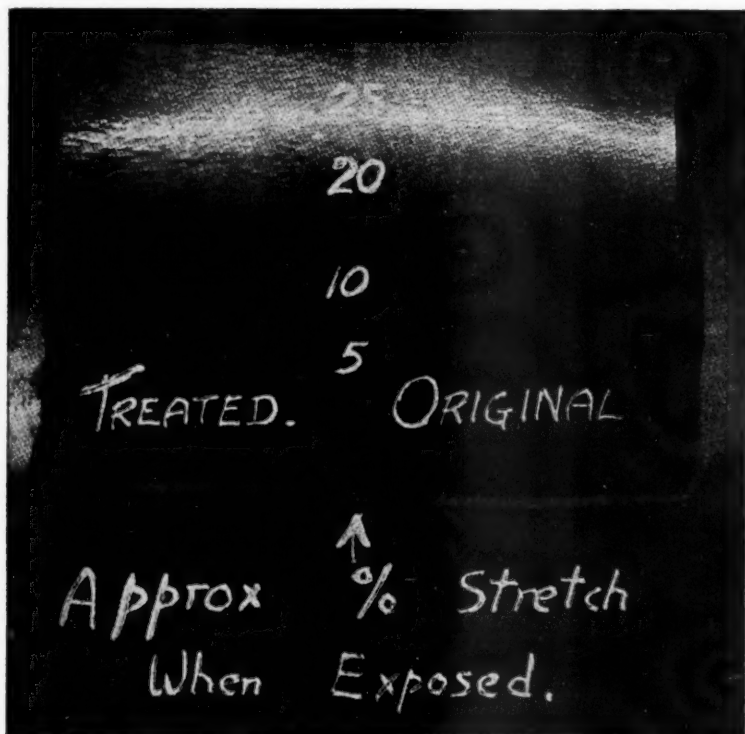


Fig. 7.—Typical result of a test on an antirack paint.

cracks which do ultimately form are produced under conditions which encourage maximum rate of development, and although such films can, and many practical ones do, delay the start of cracking, the cracking which does occur is ultimately more serious than would have been produced had no such protective coating been used.

ISOLATED DEEP CRACKING.—Cracking can be produced by causes other than deterioration by aging or exposure. The presence of grit in a slightly stressed rubber surface is an almost certain starting point of a serious deep isolated crack.

The smallness and depth of immersion of the grit controls the stage in the service life at which the crack starts. Once a crack has begun, the rate of propagation seems to be fixed solely by the stress conditions and the tearing

properties of the bulk of the material. Figure 8 shows that the rates of crack extension and cut extension are equal.

Conditions of service which produce fine cracks of small depth in highly stressed parts of a patterned rubber tire can cause those fine cracks to develop into serious deep cracks when the bolder but lower stressed parts are worn away. This is due in part to conditions changing as the section changes with wear, reducing the extreme stresses to conditions favorable to the development of a few of the deeper of the fine cracks already formed (Figures 9 and 10).

These isolated deep cracks, however produced, whether by grit, or by development from fine cracks due to changes of stress conditions, are by far the most serious forms of crack. This is because, although they are few and far between, they are large in size and serious inasmuch as they cause actual structure failure of the tire or mechanical article. The only real safeguard

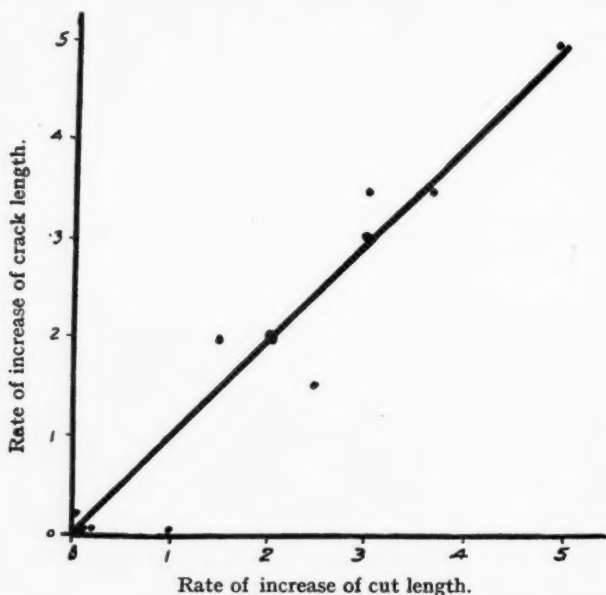


FIG. 8.—Diagram showing equality of rates of increase of cuts and cracks.

against them is to restrict their rate of propagation in depth by the use of good tear-resisting compounds. This is particularly true if the polymer is likely to be cut by external means, such as flints on tires or rubber car suspensions, for no amount of care to avoid grit or compounding for resistance to ozone can prevent such damage, and all that can be attempted is restriction of its development.

It follows that isolated deep cracking is related to ordinary fine check cracking, inasmuch as the same fundamental factors affect both types of cracking in a similar manner. The sole difference is that deep cracks are often initiated by foreign bodies when the probability of cracks occurring due to surface deterioration alone is low. It follows that the present theory covers both fine check cracking and isolated deep cracks, and the earlier idea that two separate theories were required is incorrect.



FIG. 9.—Deep cracks started by local grit compared with those developed from fine surface cracks.

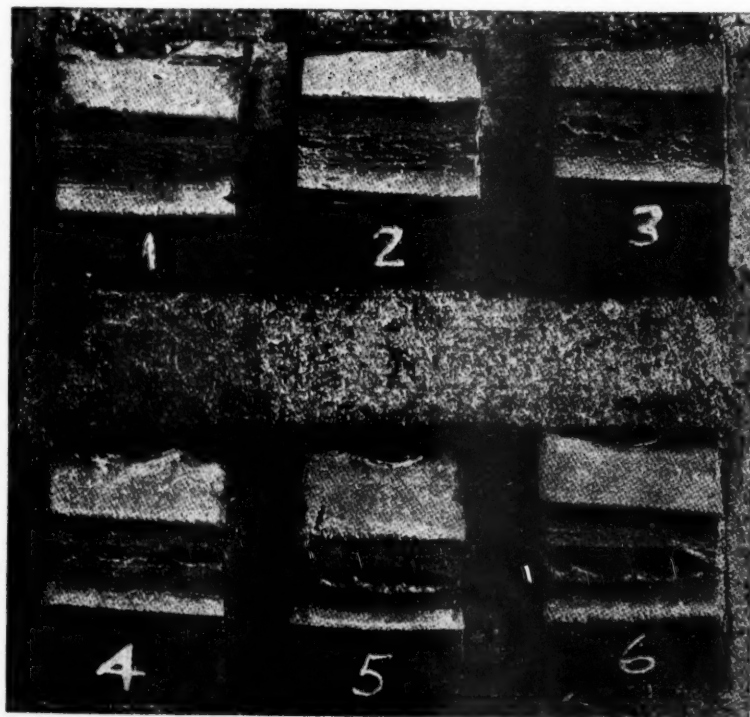


FIG. 10.—Development of deep cracks from fine cracks.

RELATIONSHIP BETWEEN RUBBER CRACKING AND METALLIC CORROSION. —It is of interest that this theory, which states that the type of cracking produced depends on the relative magnitudes of the probability of attack and rate of propagation of cracks already formed, has an important and well-established parallel in corrosion studies of metals.

Papers by U. R. Evans and others of the Corrosion Research Section at Cambridge University outline a theory³ in which the operative features are the probability of attack and conditional velocity, and are analogous to the two factors discussed by the authors. Just as in rubber cracking, these factors can be influenced in opposite directions by changes of conditions. It is of some theoretical importance that the same basic theory would appear to hold for surface deterioration of these two different substances and probably others as well.

ACKNOWLEDGMENT

Acknowledgments are gladly made to the Directors of Dunlop Rubber Co., Ltd., for permission to publish this paper, which is based on work carried out in their laboratories.

REFERENCES

- ¹ Davies and Horrabin, *Trans. Inst. Rubber Ind.* **12**, 85 (1936).
- ² Somerfield, *Trans. Inst. Rubber Ind.* **6**, 161 (1930). See Figure 46.
- ³ Evans et al, *J. Iron Steel Inst.* **149**, 67 (1944).

BEHAVIOR OF NATURAL RUBBER AND GR-S UNDER REPEATED STRESS CYCLES *

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PRELIMINARY CONSIDERATIONS

The work discussed in the present paper has been carried out on the Dunlop fatigue machine, which has been fully described by Gough and Parkinson¹. In that paper fatigue in rubber was defined as a progressive reduction of strength and resistance to tearing resulting from repeated cycles of stress under conditions such that the temperature is kept below the point where hysteresis increases (or resilience falls) with temperature rise. The actual fatigue resistance was recorded as the logarithm of the number of cycles to failure. There is, perhaps, some inconsistency between the above definition of fatigue and its quantitative measurement. The definition implies the decay of some physical properties during repeated stress cycles, but takes no account of the initial properties of the vulcanizate and the minimum value to which these must fall before internal rupture takes place. The quantitative measurement records the life of the specimen without indicating the progressive changes that occur in it during the period of the fatiguing action. It does not seem possible to evaluate strength changes in the specimen without actually rupturing it, but certain properties that change during fatigue testing are recorded at successive intervals and are taken into account in a final assessment of the compound under test. These properties include the temperature generated in the test-piece, the modulus changes which it undergoes, and the rate at which it develops permanent set.

The initial properties of the vulcanizate obviously depend on the polymer (natural rubber, GR-S, etc.), on the state of vulcanization, on the amount of stocking or aging, and on the curing and compounding ingredients (sulfur, accelerator, softeners, carbon black, etc.). The rate of decay of these properties depends on the severity of the stress cycle and on the temperature developed in the specimen; the minimum value to which tensile and tearing strength has to fall before rupture is governed by the strain put on the material and the consequent stress developed internally. The stress depends on the modulus which may (and usually does) alter as the stressing continues. If the conditions of testing and the ambient temperature are constant, the temperature of the test-piece depends on the hysteresis losses, *i.e.*, the quantity of energy converted to heat energy during each stress cycle and on the thermal diffusivity of the rubber. With most types of rubber compound, hysteresis decreases as temperature increases within the normal range of operating temperatures. If the temperature of minimum hysteresis (or maximum resilience), which varies with the polymer and with the compound, is exceeded, thermal degradation occurs and a blow-out failure is likely to result. As indicated in the above definition of fatigue, it is desirable that this critical temperature should not be exceeded during test.

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METHOD OF MIXING

A large stock of natural rubber, sulfur, accelerator, softeners and zinc oxide was made in an internal mixer and blended on a mill. Small batches were then made on a 16-inch laboratory mill, where the required amount of black was added to the common stock.

A similar stock was made with GR-S, and the carbon blacks used in this series were from the same respective lots as the black used in the natural rubber series.

The following carbons were tested in each series:—MPC (Micronex), EPC (Spheron-9), HMF (Kosmos-40) and SRF (Pelletex) at loadings of 20, 40, 60, 80 parts per 100 parts of rubber hydrocarbon. A blank or "gum" stock was included in each series. The formulas of these base stocks were:

	A (Natural rubber)	B (GR-S)
Natural rubber (N. R.)	100	—
GR-S	—	100
Stearic acid	3	1
Tackol	—	4
Zinc oxide	5	3
Sulfur	3	2
Mercaptobenzothiazole	0.85	1.5
Diphenylguanidine	—	0.3

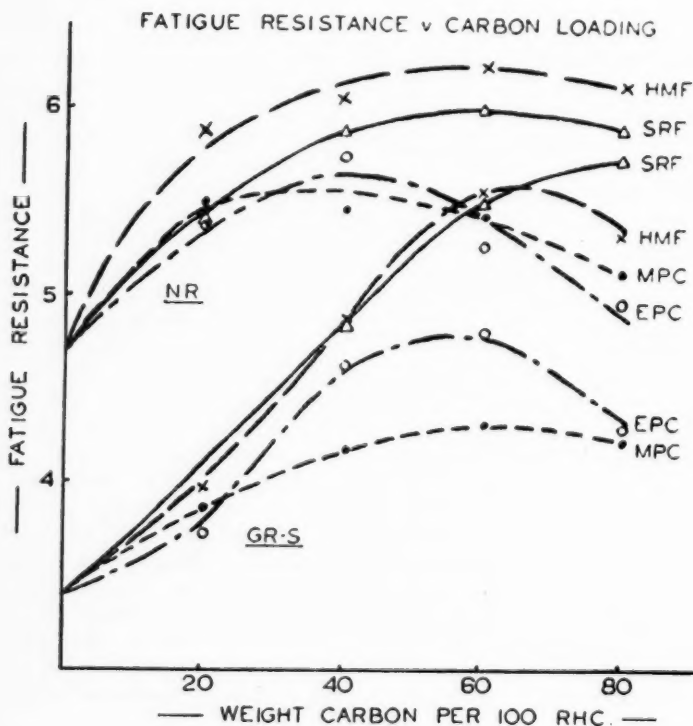


FIG. 1

TESTING CONDITIONS

The conditions of testing had to be such as to enable compounds of low resilience, such as high loaded GR-S-channel black stocks, being run without the development of overheating failures, and it was found necessary to employ smaller test-pieces than those originally described¹. The specimens now used are cylindrical blocks 60 mm. high and 40 mm. in diameter. They are thus of similar shape and exactly half the volume of those previously employed. The method of build-up is unchanged.

The tests were all made under a constant energy input of 0.4 joule per cc. In nearly all cases (except gross undercures) this enables an equilibrium temperature to be attained at which the blocks run steadily for some time before fatigue causes a breakdown internally. This steady temperature, as expected, varies within wide limits.

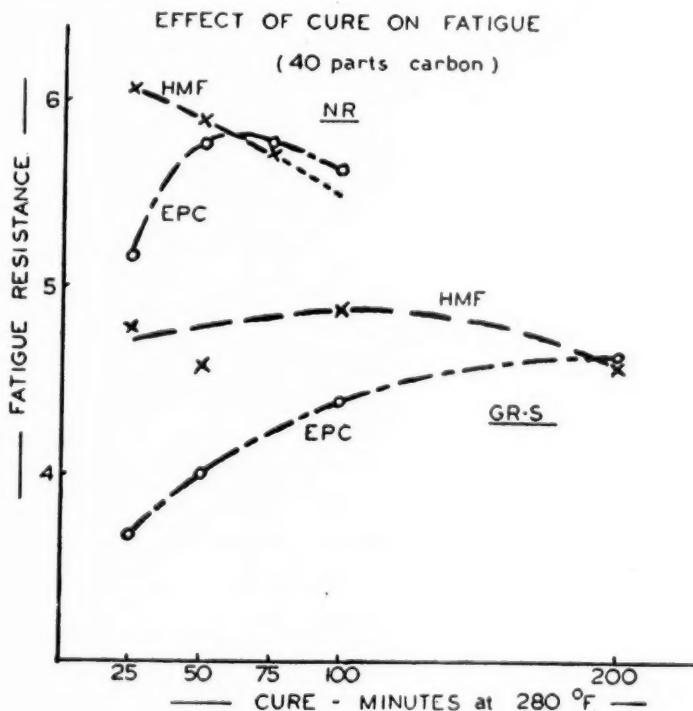


FIG. 2

COMPARISON OF NATURAL RUBBER AND GR-S

Fatigue Resistance.—Figure 1 shows that in similar type compounds natural rubber invariably resists fatigue better than GR-S. The results at optimum cure only are plotted. If, however, it be assumed that the temperature coefficient of fatigue holds over the wider range of temperatures covered by the present investigation, then the conclusion is reached that the improvement found for Hevea compounds results almost entirely from their lower running

temperatures. At equivalent temperatures the indications are that the lives of natural rubber stocks would be little longer than those of GR-S stocks. This is surprising in view of the extremely poor tensile and tear strength of GR-S at elevated temperatures compared with those of natural rubber.

The effect of time of vulcanization at 280° F on fatigue resistance of a few selected compounds is illustrated in Figure 2. It is seen that the GR-S vulcanizates run relatively better at overcures than do the Hevea vulcanizates. This results from the longer maintenance of the resilient properties with overcure by GR-S than by natural rubber (N.R.).

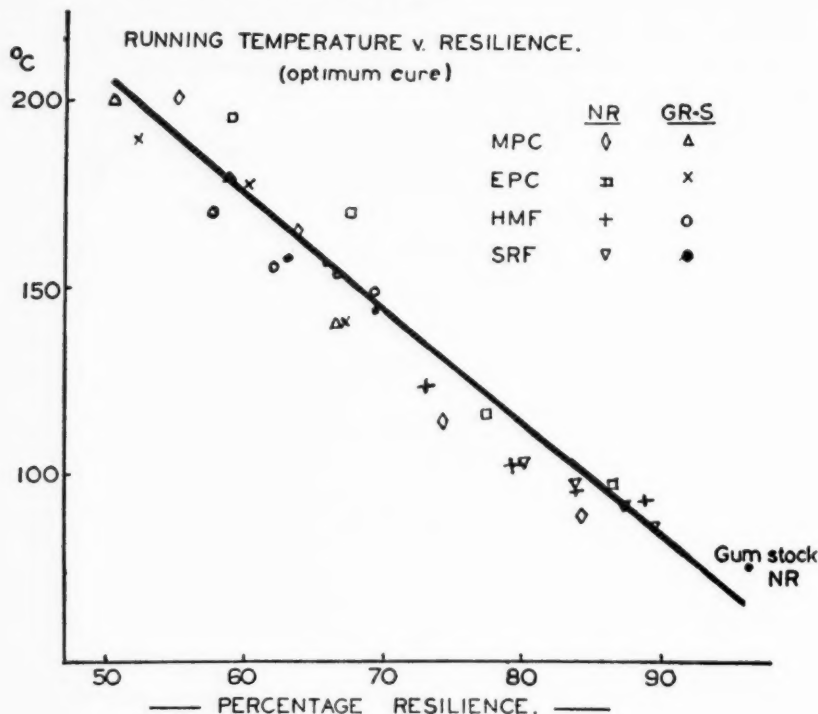


FIG. 3

Running Temperature.—GR-S compounds invariably run hotter than do similar Hevea compounds. This is due to the inherently higher hysteresis losses in GR-S. This point is brought out in Figure 3 which relates temperature development in the center of the specimen to impact resilience as measured by rebound on the Dunlop-Healey pendulum. The linear relationship which is seen to hold is to be expected, as both tests are carried out under constant energy input conditions. The graph shows that, in general, the GR-S compounds have a low rebound value and generate a high temperature on the fatigue machine.

It is a matter of experience that GR-S vulcanizates run at higher steady temperatures than do similarly compounded Hevea stocks, and in this respect they may be said to be superior to the latter. GR-S is found to have a higher resilience-temperature inversion point than Hevea, and this enables it to with-

stand higher temperatures without the development of thermal decomposition or blow-out failures. Both in the case of natural rubber and GR-S an initial temperature peak followed by an abrupt fall denotes undercure. With overvulcanized natural rubber stocks, the temperature tends to rise gradually throughout life.

Modulus.—The modulus of elasticity as measured by the fatigue test is the slope of the stress/strain curve, the stress being calculated in lbs. per sq. in. on the actual cross-sectional area at that deflection. It is constant over a wide range of deformations and hence, like Young's modulus, may be defined as the rate of increase of stress with respect to strain.

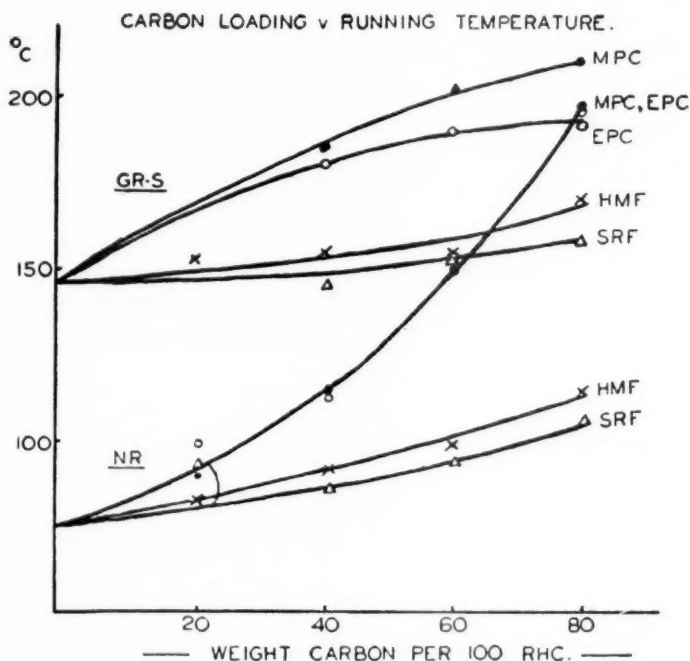


FIG. 4

In general, modulus alters as the test proceeds, the magnitude of the change depending on the state of cure and to some extent on the type of compound. Some of the tests under consideration were prolonged over periods many times in excess of those previously reported, but the conclusion that the modulus varies linearly with the logarithm of the time remains substantially true. The effect on the modulus of repeated stressing of some of the compounds studied in both natural rubber and GR-S is shown in Figures 5 and 6. It is seen that undercured specimens stiffen up during test to a greater degree than those having higher initial cures, and it often happens that if the fatigue lives are sufficiently long the final modulus of the undercured compound is higher than those at optimum and overcures. This stiffening seems to be due in part to progressive vulcanization, though it occurs at temperatures lower than those at which vulcanization normally takes place.

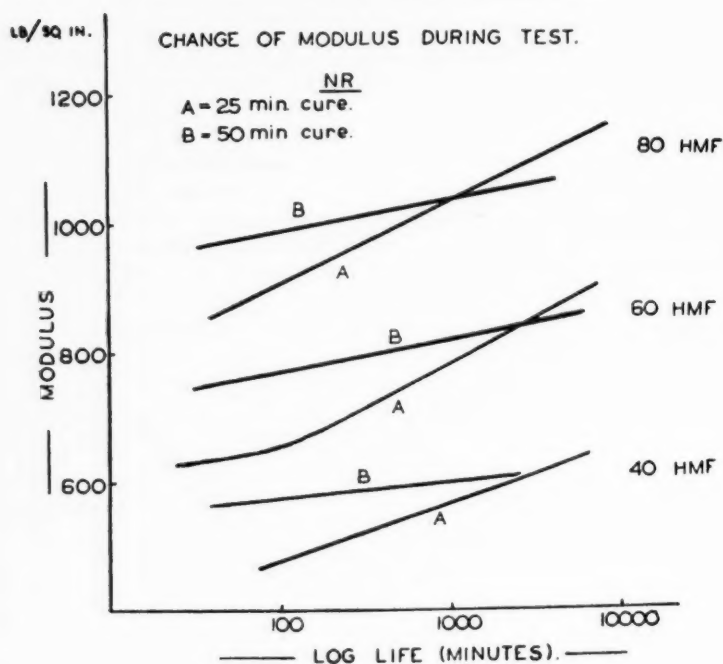


FIG. 5

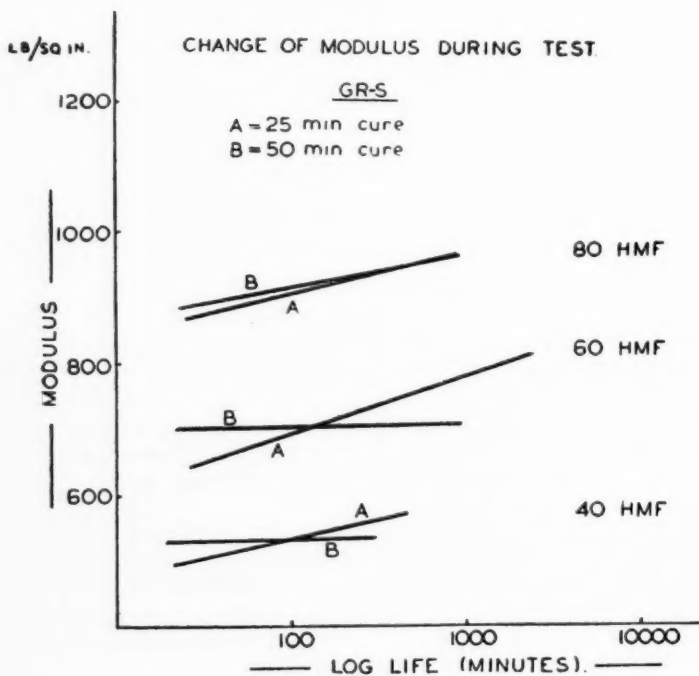


FIG. 6

Other factors influencing modulus changes have not been completely studied. Important among them is the temperature developed in the test-pieces, and it appears that the effect of high temperature and overcure combined is sometimes to cause the specimen to soften during test. The effect of compounding and curing ingredients on modulus changes needs further investigation.

There is no indication from the data accumulated in this study that GR-S stocks react differently from natural rubber stocks in respect to modulus changes during repeated stress cycles.

Changes of Dimensions.—As a result of repeated stressing the height of the test-piece decreases progressively and the block changes from a cylindrical to a barrel shape. Once the temperature has attained an approximately constant

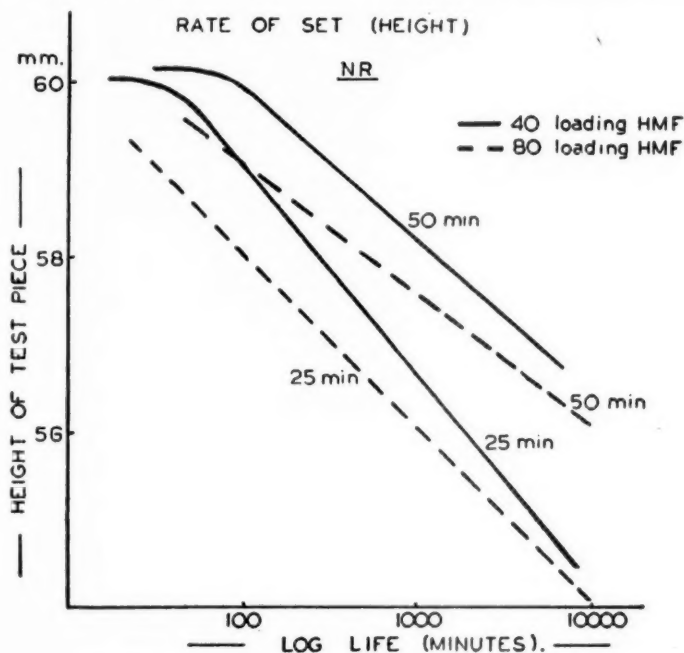


FIG. 7

value the set, measured by decrease in height, takes up a steady rate of change with respect to the logarithm of the time of test. Figures 7 and 8 illustrate changes in set of similar natural rubber and GR-S compounds. With both polymers, as the time of cure increases, the amount of set decreases, and the change to a barrel shape is less pronounced. With increasing cure the rate of set tends to decrease, but this tendency is not universal.

COMPARISON OF CHANNEL AND FURNACE BLACKS

Fatigue Resistance.—Figure 1 shows that, in both natural rubber and GR-S, (1) fatigue resistance is improved by the addition of all four grades of carbon black in any proportion up to 80 parts by weight of carbon to 100 parts of polymer; (2) there is an optimum concentration with respect to fatigue

resistance for each carbon; in general this increases as particle size increases (3) the optimum loadings in GR-S are in general higher than in natural rubber, and (4) the furnace blacks give superior fatigue resistance to the channel blacks in both Hevea and GR-S.

Running Temperature.—As expected, the temperature in the interior of the test-piece increases in a regular manner with carbon concentration and, among the four blacks under consideration, with decreasing particle diameter. Figure 4 relates running temperature at optimum fatigue resistance to black loading. The most striking feature is the rapid increase in temperature with loading of the natural rubber-channel black compounds. At the 80 parts loading these compounds ran nearly as hot as the corresponding GR-S stocks.

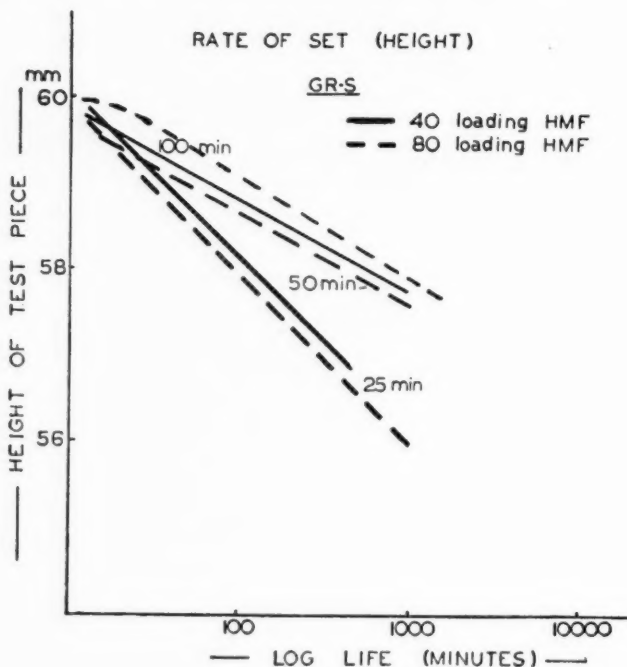


FIG. 8

Modulus.—The curves relating initial modulus to carbon concentration for both natural rubber (Figure 9) and GR-S (Figure 10) show rather surprisingly that EPG has a greater stiffening effect than MPC. The relationship between initial modulus and hardness (British Standard) of natural rubber compounds is shown in Figure 11. For the same modulus the hardness diminishes according to the type of black in the compound in the order: MPC, EPC, HMF. With GR-S compounds a similar relation holds, but the channel black curves are closer together (Figure 12). It should be noted that the hardness is a measure of the deformation of a rubber sample under a given (relatively small) load, and therefore has an arbitrary value. Modulus, on the other hand, as determined on the fatigue machine, is a ratio, and is independent of the applied stress.

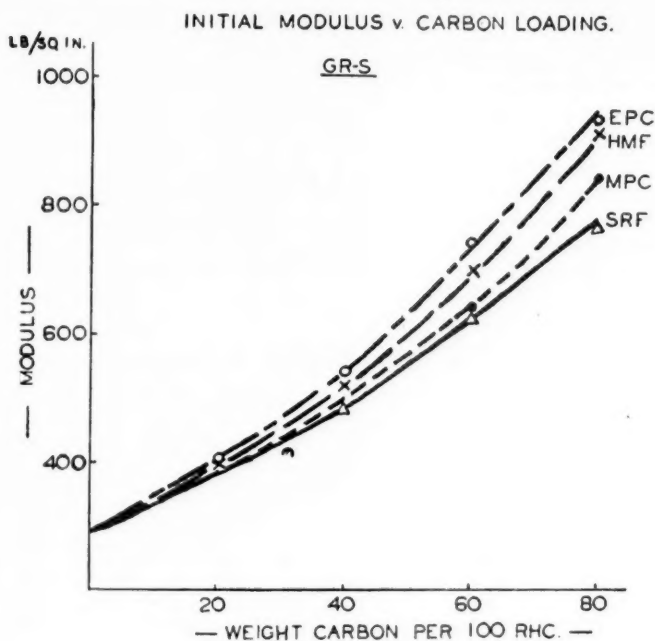


FIG. 9

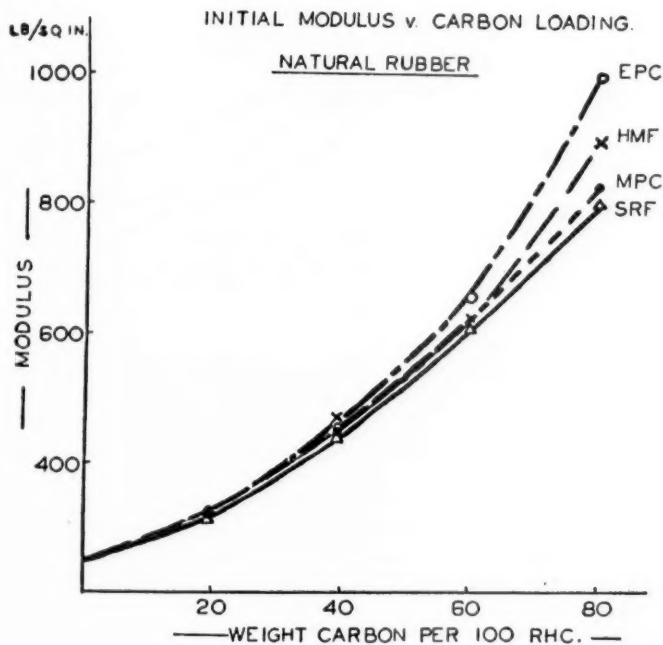


FIG. 10

CONCLUSIONS

Vulcanized Hevea rubber resists fatigue better than the butadiene-styrene copolymer GR-S, but not to the extent that might be expected from its superior tensile and tear strengths and its higher resilience. The incorporation of all types of colloidal carbon normally used for reinforcing both natural rubber and GR-S increases the resistance to fatigue of the vulcanizate to a greater or less degree, despite the fact that such compounds develop higher temperatures under constant energy input conditions than do the unloaded (gum) stocks. The high modulus and semireinforcing blacks impart better resistance to fatigue than do the channel blacks, which run at higher temperatures.

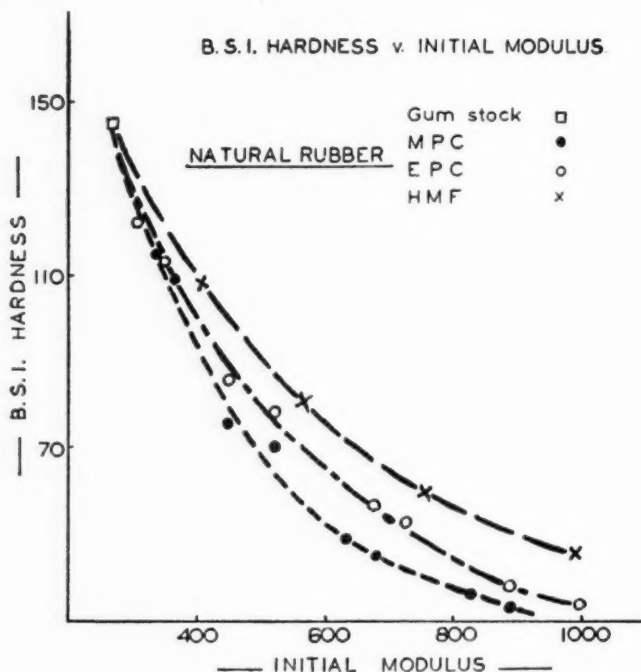


Fig. 11

The evidence as a whole points to the conclusion that fatigue resistance is influenced positively by the reinforcing action of the carbon and negatively by its adverse effect on resilience. Thus the high hysteresis losses in the channel black compounds more than offset the reinforcing effect, and better results are obtained by the use of carbons with larger particles. Further work is needed to determine the type of carbon which gives the best compromise between these opposing tendencies. The indications are that carbon black particles with diameters in the range 45 to 80 μ are likely to give the greatest resistance to fatigue under constant work conditions. The effect on fatigue of carbon structure superimposed on that of particle size influences the results to a degree not yet determined.

ACKNOWLEDGMENT

Acknowledgments are gratefully made to J. S. Bates and members of the testing section for help, and to the Directors of the Dunlop Rubber Co., Ltd. for permission to publish the results of the investigation.

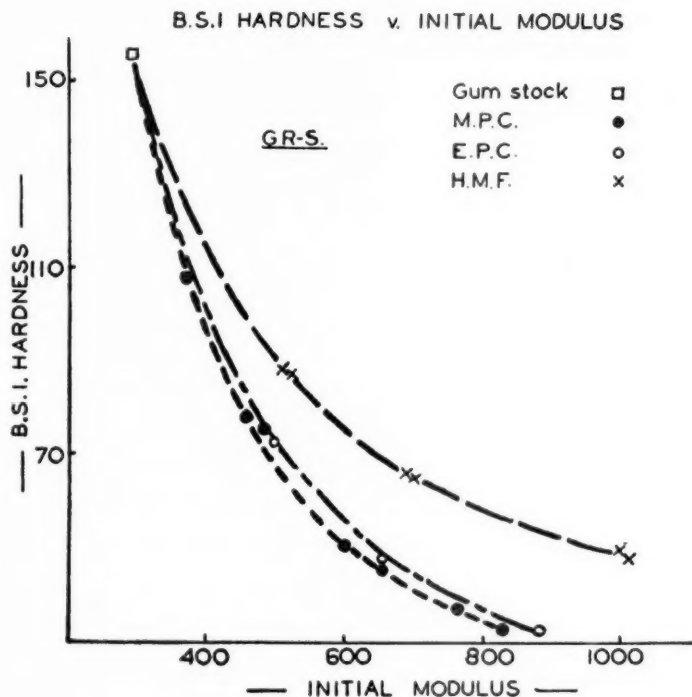


FIG. 12

REFERENCE

Gough and Parkinson, *Trans. Inst. Rubber Ind.* **17**, 168 (1942).

ELECTROSTATIC AND TENSILE PROPERTIES OF RUBBER AND GR-S AT ELEVATED TEMPERATURES *

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In a previous paper¹ a new apparatus for measuring the electrostatic contact potential of rubber and GR-S compounds was described, and a correlation of tensile strength and electrostatic contact-potential was observed. This work resulted in the formulation of an "electrostatic contact potential theory of reinforcement", in which reinforcement is explained on the basis of electrical contact potentials and resultant electrostatic attractive forces set up between the rubber and the reinforcing agents. For example, when a material which has a positive electrostatic charge, such as zinc oxide, is added to rubber, which has a negative charge, strong electrostatic attractive forces are set up between the zinc oxide and the rubber, and give rise to reinforcement. Now since positive and negative charges tend to neutralize each other, the electrostatic contact potential or electrical charge on the resulting stock should be more positive than it was before addition of the zinc oxide. This was found to be the case; and in general, the more positive the stock, the higher the tensile strength.

On the basis of this theory, we would predict that rubber compounds when heated would become highly negative, which would indicate a low hot tensile strength. This was found to be the case.

It is the purpose of this paper to describe a new apparatus for measuring contact potentials at elevated temperatures, and to point out that the contact potentials of both rubber and GR-S compounds become highly negative at 212° F. This increase in negative potential, which may be a "boiling off" of electrons and resultant disruption of electrostatic attractive forces within the material, is much greater for GR-S than for rubber, probably accounts in part for the much greater decrease in tensile of GR-S over rubber at elevated temperatures, and is further confirmation of the electrostatic contact potential theory of reinforcement.

By the application of this theory, materials which maintain their highly positive charge at elevated temperatures should make the GR-S stocks more positive, prevent the release of electrons, and increase the hot tensile strengths. This was found to be the case; and certain materials such as proteins, finely divided silica and sodium silicate when added as water dispersions to GR-S latex gave products having considerably improved tensile strengths at elevated temperatures.

HIGH-TEMPERATURE CONTACT POTENTIAL APPARATUS

To measure contact potentials at elevated temperatures, the rubber test-specimen must be heated to the desired temperature on an electrically insulated

* An original contribution.

surface, momentarily contacted with a cold reference surface (preferably polished steel), and instantly separated therefrom. The electrical charge or contact potential then can be measured on either the rubber test-specimen or on the standard reference contacting surface, since the charges are equal and opposite. In our previous apparatus¹ an insulated steel plunger contacted the test-specimen, and the charge was measured on the test-specimen, which was mounted in a sample holder built into the electrostatic modulator. In this apparatus, it is difficult to build the electrical heater around the sample and provide adequate electrical shielding to prevent the hot a.c. electrical fields around the heater from being picked up on the grid of the audio amplifier. Furthermore, the charged plunger should be out of the test-specimen's high-temperature electrostatic field when measurements are made. The modulator unit should be isolated from the hot electrostatic field around the sample. To take care of these difficulties, a new apparatus was designed.

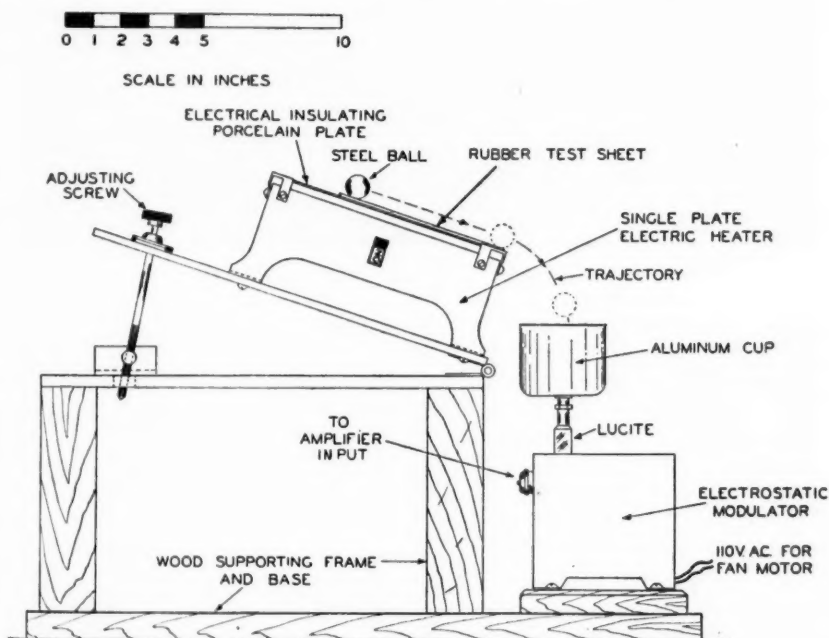


FIG. 1.—Rolling ball contact-potential apparatus.

ROLLING BALL CONTACT POTENTIAL APPARATUS

In this apparatus (See Figure 1 and Figure 2), the electrostatic charge, acquired by rolling a steel ball down the surface of a rubber test-specimen on a heated inclined plane, is measured when the ball drops into the cup of a suitable measuring device, such as our electrostatic modulator.

The electrostatic modulator (See Figure 3) was described completely in our previous paper¹. Briefly, it consists of a motor-driven fan which cuts the electrostatic field produced by the charged sample and converts it into an alternating current voltage which easily is amplified and measured by the asso-

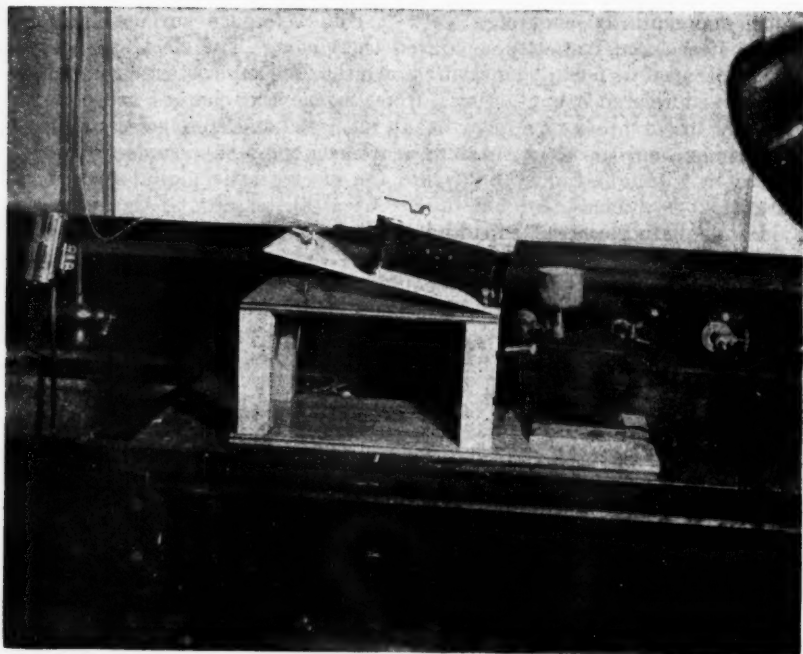


FIG. 2.—Rolling ball contact-potential apparatus.

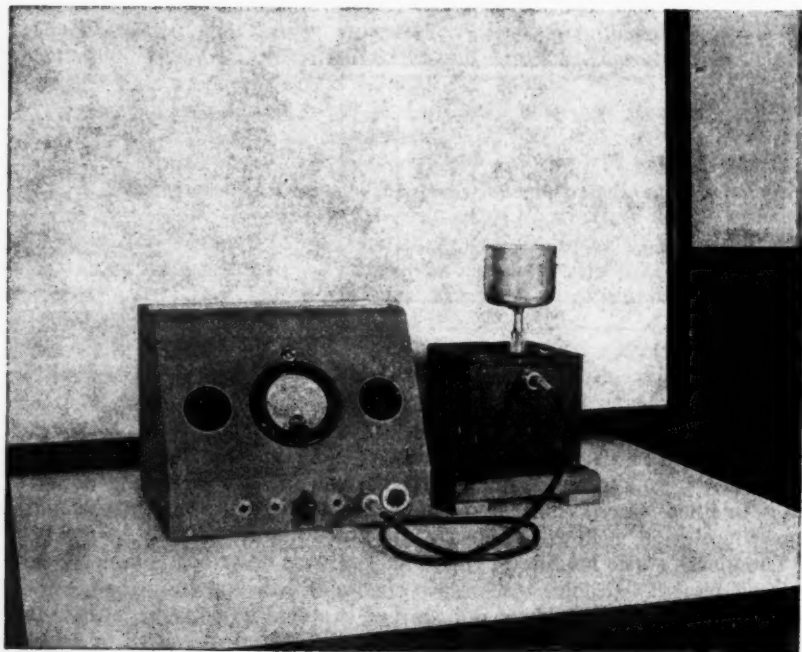


FIG. 3.—Electrostatic modulator with audioamplifier and output meter.

ciated audiofrequency amplifier and built-in output meter. The electrostatic modulator and amplifier were calibrated with an adjustable d.c. high-voltage power supply. The power supply leads were attached to the modulator cup and chassis. Amplifier output meter readings were plotted against input volts from the d.c. power supply. The contact-potential values reported are all in terms of these input volts. These contact-potential values are not the actual contact potentials since they depend on the capacity of sample, capacity of modulator system, and a number of other factors; however, they are proportional to the actual contact-potentials of the rubber test-specimens.

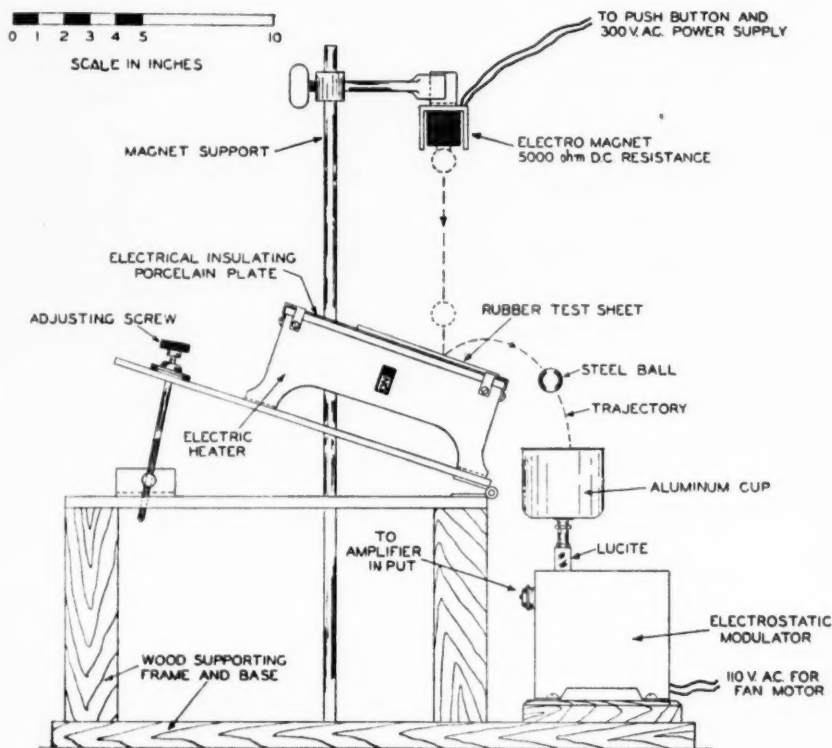


Fig. 4.—Bouncing ball contact-potential apparatus.

With this apparatus, the test-specimen is both shielded and electrically insulated from the heater by means of the porcelain enameled steel top-plate. The charged steel ball which contacts the specimen is isolated from electromagnetic and electrostatic fields when measurements of its charge are made in the shielded electrostatic modulator unit. While this apparatus has a number of advantages over the plunger type apparatus for high temperature measurements, it also has some disadvantages. The contact area and velocity of the ball as it leaves the sample are not constant for all samples. For example, a soft stock has a greater contact area than a hard one, and a stock with a tacky surface retards the velocity of the ball, which affects the speed of separation of the ball from the test-specimen. Since both of these factors affect the contact-

potential values, they must be taken into account in testing unknown compounds. For similar compounds, these differences usually do not exceed 10 per cent error. The relative contact area can be estimated approximately by coating the steel ball with "fingerprint" ink and measuring the length and width of the black streak thus produced. The relative velocity of the ball as it leaves the sample can be estimated from its trajectory. The greater the velocity of the ball, the greater is the horizontal range on the trajectory curve. This distance can be easily measured from the imprint of the ball on carbon over white paper.

MECHANICS OF ROLLING BALL CONTACT-POTENTIAL APPARATUS

The mechanics of the rolling ball apparatus along with the derivation of the formula relating horizontal range (S) to velocity (V) are of theoretical interest, and have been calculated by L. E. Carlson of our Research Laboratories as follows: Refer to Figure 5.

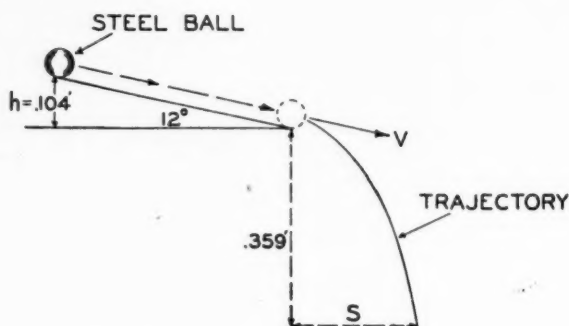


Fig. 5.—Mechanics diagram of rolling ball apparatus.

1. Total Area of Contact

Length of streak = 6 inches.

Width of streak = $1/16$ inch.

Area = $6 \times 1/16 = 0.375$ sq. inch.

2. Pressure

Weight of ball = 0.0544 lb.

Dia. of ball = $23/32 = 0.718$ inch.

Dia. of contact = $1/16$ inch.

Instantaneous area of contact = $(1/32)^2 \pi$ sq. inch.

Pressure = $0.0544 / (1/32)^2 \pi = 17.8$ lbs. per sq. in

3. Velocity

Assume that potential energy of ball at top of incline is converted into rotational and translational kinetic energy by the time it reaches the bottom of the incline of height (h). Thus:

$$mgh = 1/2 mV^2 + 1/2 IW^2$$

Substituting values of I and W the energy equation reduces to

$$mgh = 1/2 mV^2 + 1/5 mV^2$$

m = mass of ball

h = height of incline (0.104')

g = acceleration of gravity

$$V = \sqrt{\frac{10gh}{7}}$$

$$V = \sqrt{10 \times 32.2 \times \frac{0.104}{7}} = 2.19$$

ft. per sec.

V = translational velocity (at bottom of incline) parallel to it.

I = moment of inertia
 $= \frac{2}{5} mr^2$ where r is radius of ball

W = rotational velocity = V/r

V is the maximum velocity obtainable, assuming the ball rolls and does not slide. Actually, tackiness of the surface and indentation of the surface slow the ball somewhat.

The following is a means of determining actual velocity from horizontal range which is the horizontal distance the ball moves while in the air.

RELATION OF VELOCITY TO DISTANCE (S)

Assuming the ball starts the trajectory path with a velocity V and travels the horizontal distance (S) and the vertical distance 0.359 ft. in time t , the following equations of motion may be set up.

$$0.359 = \frac{1}{2}gt^2 + V \sin 12^\circ t$$

$$S = V \cos 12^\circ t$$

Eliminating t and solving for V :

$$V = \frac{4.11 \times S}{(0.359 - 0.2126S)^{0.5}} \text{ ft. per sec.}$$

Since S can be measured experimentally, V can be calculated by the above formula.

BOUNCING BALL CONTACT-POTENTIAL APPARATUS

To secure a more intimate contact between the steel ball and the test-specimen, the "bouncing ball" type apparatus was designed (refer to Figure 4). In this apparatus, which is in part similar to the rebound apparatus described in a previous paper², the steel ball is held above the test-specimen by means of an electromagnet and is dropped upon the rubber test-specimen, which is mounted on a heated inclined plane. The ball bounces into the electrostatic modulator where its charge is measured. With this apparatus, the work done on the sample during a test is so great that there is some evidence that it brings about a structural change in the rubber. In any case, repeated tests on the same spot in the rubber show a progressive decrease in charge (stocks become more positive), which would indicate an increase in tensile strength.

MECHANICS OF BOUNCING BALL CONTACT-POTENTIAL APPARATUS

The mechanics of the bouncing ball apparatus are of theoretical interest and are given as follows: Refer to Figure 6.

1. Area of Contact

Diameter of contact spot = 0.25 inch.

Determined experimentally by coating ball with fingerprint ink.

Area = $(0.125)^2 \pi = 0.049$ sq. inch.

2. Pressure

Dia. of ball = 0.718 inch.

Wt. of ball = 0.0544 lb.

Dia. of contact spot = 0.25 inch.

Depth of penetration = X .

$$X = 0.359 - \sqrt{(0.359)^2 - (.125)^2}.$$

$$X = 0.022 \text{ inch.}$$

The ball falls 7.25 inches on to the rubber. It penetrates the surface a depth X . From the law of conservation of energy, it can be shown that the weight of the ball times the distance it falls equals the force exerted on the rubber times the depth of penetration X .

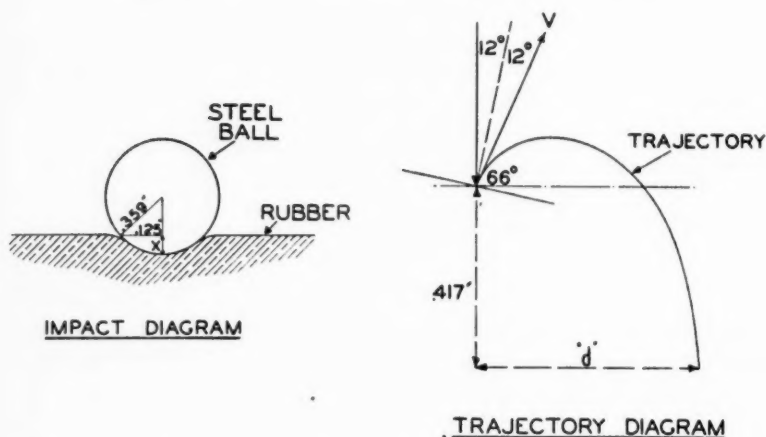


FIG. 6.—Mechanics diagram of bouncing ball apparatus.

Thus:

$$0.0544 \times 7.25 = F \times 0.022.$$

$$F = 17.9 \text{ lbs.}$$

$$\text{Pressure} = \frac{17.9}{0.049} = 365 \text{ lbs. per sq. in.}$$

3. Velocity

If the rubber stocks were 100 per cent resilient, the velocity of the ball leaving the stock would be equal in magnitude to the velocity of the ball falling 7.25 inches from rest.

$$V = \sqrt{2gs} = \sqrt{\frac{2 \times 32.2 \times 7.25}{12}}$$

$$V = 6.24 \text{ ft. per sec.}$$

This is the maximum velocity obtainable. Since resilience is proportional to kinetic energy regained after rebound, and kinetic energy is proportional to

velocity squared, it can be shown that actual velocity after rebound is as follows:

$$V = 0.624\sqrt{R} \text{ ft. per sec.}$$

Where R is resilience in percentage.

Another means of measuring this velocity is by the use of d , the horizontal distance the ball moves after bouncing. If the ball starts with a velocity V (as shown in Figure 6) and falls a distance of 0.417 feet in time t , equations of motion can be set up.

Assuming the angle of impact equals the angle of rebound, these equations are:

$$V \sin 66^\circ t + 1/2gt^2 = 0.417$$

$$V \cos 66^\circ t = d$$

Solving for V in terms of d

$$V = \frac{10.1d}{\sqrt{0.417 + 2.246d}} \text{ ft. per sec.}$$

Values of V obtained from this formula agreed with values obtained from the resilience—velocity formula within about 5 per cent. Hence, the assumption of equal angles has experimental justification.

TESTING PROCEDURE

A $6 \times 6 \times 0.075$ inch tensile sheet³ cured in a clean chromium-plated mould is used for test. The carefully prepared specimen¹, whose surface should be free from dust, lint, surface bloom or other foreign matter and free from electrical charge, is placed on the inclined plane and brought to the desired testing temperature by proper adjustment of the Variac supplying the current for the electric heater. Temperature can be measured by means of a thermocouple placed on the stock and another built into the top surface of the inclined plane. A four-minute heating period is usually required to bring the tensile sheet to a testing temperature of 212° F. The steel ball (ballbearing) which is used to contact the sample is first cleaned with pure acetone. The ball is then picked up and gently placed on top of the rubber test sheet and allowed to roll freely down the rubber on the incline and drop into the cup of the electrostatic modulator, where its charge is measured on the output meter of the audio amplifier. This test is repeated several times, taking care to roll the ball over a fresh uncontacted surface each time. The test-specimen should be placed slightly over the lower edge of the inclined plane so that arcing and resultant discharge of the ball cannot take place between the ball and the metal of the heater.

The specimen preparation and test procedure for the bouncing ball apparatus are the same as for the rolling ball apparatus, with the exception that in the former the ball is released from an electromagnet and bounced instead of rolled into the electrostatic modulator. A thicker test-specimen is sometimes desirable with this apparatus, and samples 0.20 inch thick were used for certain tests. All contact potential measurements must be made in a constant temperature, constant humidity room; 78° F and 45 per cent relative humidity testing conditions have been found to be satisfactory. Like all electrostatic work, results are difficult to duplicate, and a large number of tests must be run.

EXPERIMENTAL DATA

INCREASE OF CONTACT-POTENTIAL WITH TEMPERATURE

Our electrostatic contact potential theory of reinforcement predicts that GR-S should become highly negative at elevated temperatures to explain the low hot tensile strengths of GR-S. To check this, contact potentials were run at 78° F and 212° F on a 20-volume zinc oxide loaded GR-S stock and also on a similar rubber stock. Data were obtained with both the rolling ball and bouncing ball contact-potential equipment. Rebound data were also obtained using the St. Joe inclined-plane falling ball rebound tester². Hot tensile data were obtained with the St. Joe electric heater attachment⁴ for the Scott tensile machine (See Figure 7). These data are shown in Table I. The zinc oxide

TABLE I
COMPARISON OF ROLLING-BALL AND BOUNCING-BALL ELECTROSTATIC
CONTACT-POTENTIALS OF RUBBER AND GR-S

Test	GR-S Formula A		Rubber Formula B	
	78°F	212°F	78°F	212°F
Electrostatic contact potential* (volts)				
1. Rolling ball apparatus	116	293	103	140
2. Bouncing ball apparatus	36	89	28	37
Tensile strength (lbs. per sq. in.)	1000	115	3500	2100
Elongation (percentage)	930	400	620	625
Modulus at 400% (lbs. per sq. in.)	125	115	1200	—
Rebound (percentage)	35	36	44	56
Shore hardness	42	—	51	—
Rex hardness	44	—	53	—

Formulas			
A		B	
GR-S	100	Rubber	100
Sulfur	2.5	Sulfur	3.5
Mercaptobenzothiazole	1.5	Mercaptobenzothiazole	0.6
Zinc oxide	113	Stearic acid	1.5
	—	Zinc oxide	113
	217.0		—
			218.6
Cure 55 min. at 280° F.		Cure 35 min. at 280° F.	

* The contact potential values are in terms of negative input volts at modulator. The smaller the value, the more positive the potential.

used in these and all subsequent tests was a fine particle size (0.2 micron average diameter), fast-curing type produced by the St. Joe electrothermic process. It will be noted that the GR-S contact potential increased about 150 per cent while the rubber contact potential increased less than 50 per cent. This was true for both the rolling and bouncing ball type apparatus. These data checked the theory, and it was decided to repeat these tests and run additional ones at different temperatures on both high-zinc and pure-gum rubber and GR-S stocks. Since the bouncing ball apparatus gave such low contact-potentials because of the small contact area, the results were difficult to check, and all subsequent tests were run only with the rolling ball apparatus. These contact-potential data are shown in Table II. The tensile data are shown in Table III. It will be noted that in all cases there is an increase in negative contact-potential as the temperature is increased. This corresponds with a decrease in

tensile strength with temperature, and is further confirmation of the electrostatic contact potential theory of reinforcement.

It is interesting to note that the high contact-potential values observed at elevated temperatures tend to persist for a short time after the stock is cooled, indicating an alignment or orientation of charges such as a semipermanent polarization of the stock.

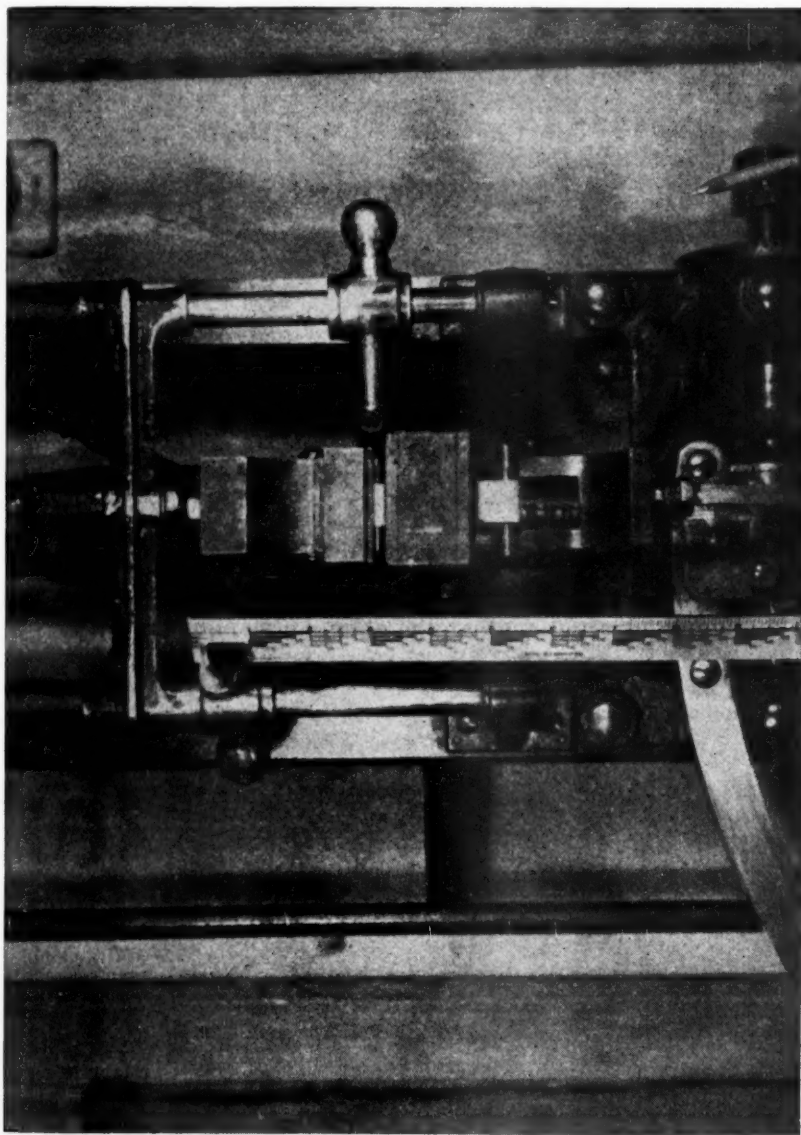


FIG. 7.—St. Joe hot tensile apparatus.

TABLE II
EFFECT OF TEMPERATURE ON ELECTROSTATIC CONTACT POTENTIALS OF RUBBER AND GR-S

See Table I for formulas A and B

See Table I for formulas A and B											
Formula	Composition	Minutes cure at 280°F	Electrostatic contact potentials Rolling ball apparatus (volts)					Rebound (percentage)		Hardness 78°F	
			78°F	145°F	212°F	278°F	78°F	212°F	Shore (max.)	Rex	
C	Pure-gum rubber	35	100	120	150	250	48	59	42	43	
D	Pure-gum GR-S	55	150	225	325	450	42	43	35	35	
B	Rubber with 20 vols. zinc oxide	35	85	115	140	185	44	56	51	53	
A	GR-S with 20 vols. zinc oxide	55	115	200	285	400	35	36	42	44	
Formulas											
C			D								
Rubber		100	GR-S					100			
Sulfur		3.5	Sulfur					2.5			
Mercaptobenzothiazole		0.6	Mercaptobenzothiazole					1.5			
Stearic acid		1.5	Zinc oxide					5.			
Zinc oxide		5.						<hr/> 109.0			
		110.6									

TABLE III
EFFECT OF TEMPERATURE ON TENSILE OF RUBBER AND GR-S COMPOUNDS

See Tables I and II for Formulas A, B, C and D

Formula	Composition	Cure (min. at 280°F)	78°F			145°F			212°F			270°F		
			Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)
C	Pure-gum rubber	35	3350	775	315	2850	675	400	2200	760	275	160	250	—
D	Pure-gum GR-S	55	145	450	75	85	250	—	50	150	—	25	160	—
B	Rubber with 20 vols. zinc oxide	35	3500	620	1200	2850	640	750	2300	625	500	465	400	465
A	GR-S with 20 vols. zinc oxide	55	1000	930	125	225	500	150	125	425	100	65	275	—

ADDITION OF POSITIVE (+) MATERIALS TO GR-S
TO INCREASE HOT TENSILE STRENGTHS

A number of materials having, in effect, a less negative electrostatic contact-potential were added to GR-S to make it less negative at elevated temperatures and, according to the theory, to increase its tensile strength. Some of these materials, such as Flectol-H, while positive and effective in increasing tensile strength at room temperatures, became highly negative at elevated temperatures, and for this reason, neither made the stocks more positive nor increased their tensile strengths at elevated temperatures. A few of these materials when properly dispersed maintained their positive charges at elevated temperatures, making the GR-S less negative and giving increased stocks with greater tensile strengths. These materials were finely divided SiO_2 , Na_2SiO_3 and certain proteins such as egg white. These materials were not effective when milled into GR-S, and did not change appreciably the contact potentials or tensile strengths. A careful examination of the stocks showed poor dispersion of all of these materials. To obtain effective dispersions, these materials were dispersed in water and the water dispersions were added to GR-S latex. The procedure was as follows.

LATEX DISPERSIONS

To 1000 grams of Type II GR-S latex (30 per cent solids) were added water dispersions of the positive materials in such an amount as to give 20 per cent on the GR-S solids. Then, 600 grams of 50 per cent Black Label No. 20 zinc oxide, dispersed in water with 1 per cent of Stablex-B, was added. Coagulation was carried out by the addition of 100 to 200 cc. of 28 per cent Epsom salt solution. Egg white and especially sodium silicate are good dispersing agents for zinc oxide and act as stabilizing agents, making it difficult to coagulate the latex. After coagulation, the material is dried at 190°F for approximately twenty-four hours or until the moisture content is under 0.35 per cent. The resulting GR-S master batch contains approximately 50 per cent of zinc oxide and 20 per cent (on GR-S) of the added positive material. Compounding then was carried out and regular milling procedure followed in basic Formula E. Formula E is similar to Formula A, except that it contains 18 volumes of zinc oxide instead of 20 volumes.

FORMULA E

	Parts by weight
50% Zinc oxide master batch from GR-S latex (Spec.)	200
Sulfur	2.5
Mercaptobenzothiazole	1.5
	<hr/> 204.0

The tensile strength, rebound, and contact-potential data are shown in Table IV. It will be noted that these materials markedly increased the contact potential (made it more positive) and increased both the room-temperature tensile strength and the hot tensile strength of GR-S. The hot tensile strength is more than doubled for the egg white (albumen) and sodium silicate stocks. Modulus, hardness, and rate of cure also are increased, while rebound values are of the same order. The stocks containing egg albumen were different from any of the other stocks in that they milled out extremely smoothly

TABLE IV
ADDITION OF POSITIVE MATERIALS TO GR-S LATEX

Composition	Cure (min. at 280°F)	Electrostatic contact- potentials (volts)		Original tensile strength (78°F)			Tensile strength at 212°F			Rebound (percentage)		Hardness 78°F Shore (15 sec.)
		78°F	212°F	Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elon- gation (per- centage)	Modulus at 400% (lbs. per sq. in.)	78°F	212°F	
Standard	50	100	275	900	850	225	150	300	—	36	37	40
20% Egg white	20	93	180	1475	538	1000	400	250	—	37	40	49
20% SiO ₂	50	95	195	1325	990	200	300	400	300	33	34	37
20% Na ₂ SiO ₃	40	90	175	1475	450	1200	400	200	—	36	39	49

Positive Materials Added

2 egg whites added to 1000 grams of Type II GR-S latex (30% solids)
400 grams of 15% Santocel (SiO₂) dispersed in water
120 grams of 50% sodium silicate in water

Basic Formula E (see text)

and gave a long, plastic, uncured sheet when taken from the mill. They resembled natural rubber more in this respect than any other GR-S material we have observed.

DISCUSSION OF RESULTS

To show the relations between temperature, contact potential, and tensile strength, additional data were obtained at various temperatures on the standard latex compound containing no sodium silicate and on one containing 20 per cent of sodium silicate. These data are shown in Table V, and have been

TABLE V
EFFECT OF TEMPERATURE ON GR-S CONTAINING SODIUM SILICATE

Temperature of test	Tensile strength							
	Contact potential (volts)		Standard stock No sodium silicate			20% sodium silicate		
			Tensile strength (lbs. per sq. in.)	Elongation (percentage)	Modulus at 400% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	Modulus at 400% (lbs. per sq. in.)
	Standard stock	20% Na ₂ SiO ₃ stock						
78° F	100	85	900	850	225	1475	475	1000
145° F	180	125	500	400	300	890	425	700
212° F	275	185	150	300	—	400	200	—
279° F	410	255	50	150	—	275	225	—
Basic Formula E								

Basic Formula E

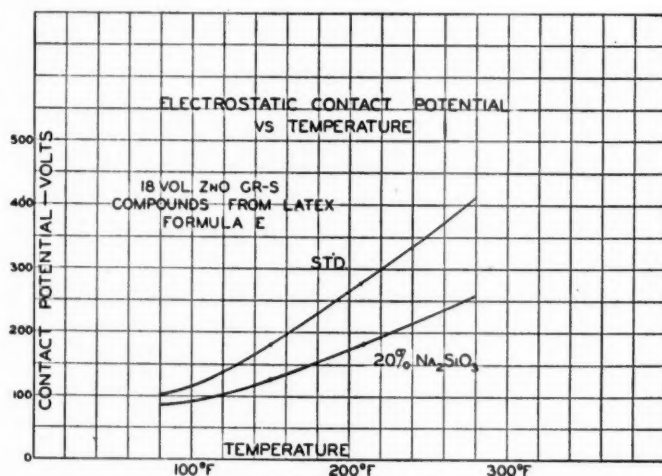


Fig. 8.—Contact potential vs. temperature for sodium silicate stocks.

plotted in the form of curves (Refer to Figures 8 and 9). Figure 8 shows the increase in contact potential with temperature and also that the addition of Na_2SiO_3 greatly decreases the contact potential and makes the stock more positive. Figure 9 shows how the tensile strength drops off with temperature and shows the superiority of the Na_2SiO_3 stock.

In Figure 10, the contact potential data for all the rubber compounds run at different temperatures have been plotted against the tensile strength values; and it appears that there is a relation between tensile strength and contact potential.

In Figure 11, the contact potential data for all the GR-S and GR-S latex compounds run at different temperatures have been plotted against the corresponding tensile strength values, and again it appears that there is a correlation of contact potential and tensile strength; however, it is a different one from that

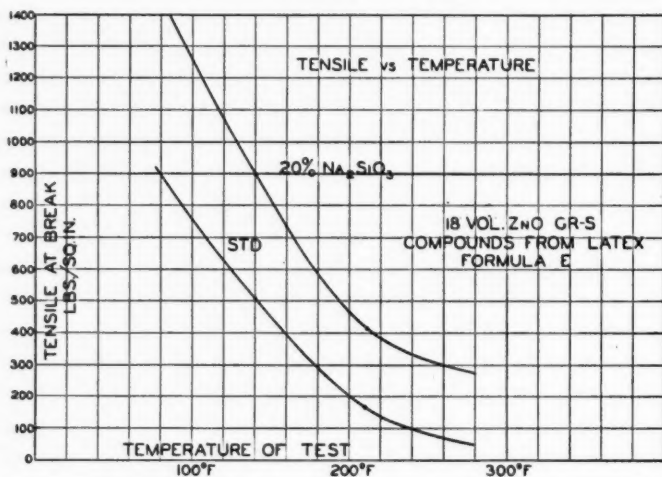


Fig. 9.—Tensile vs. temperature for sodium silicate stocks.

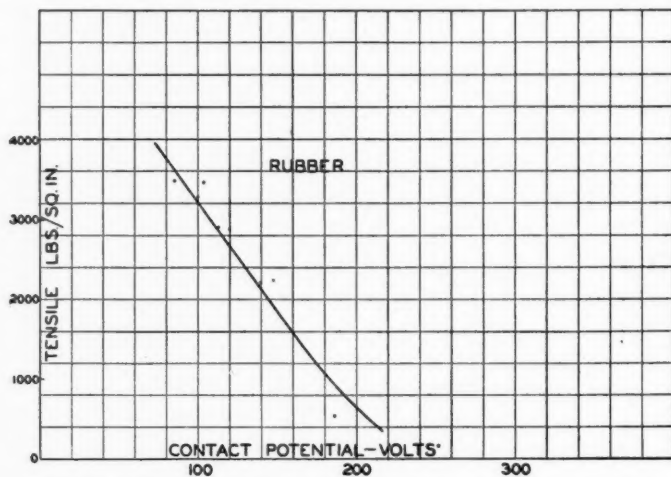


Fig. 10.—Contact potential vs. tensile strength for all rubber compounds.

for rubber, as might be expected from the difference in physical and chemical properties of the two materials. These data are all further confirmation of the electrostatic contact-potential theory of reinforcement.

SUMMARY AND CONCLUSIONS

A new apparatus has been described for measuring contact potentials of rubber and GR-S compounds at elevated temperatures. In this apparatus, the

electrostatic charge, acquired by rolling a steel ball down the surface of a rubber test-specimen on a heated inclined plane, is measured when the ball drops into the cup of an electrostatic modulator. This potential, although not the actual contact potential, is nevertheless, proportional to it. With this apparatus, the contact potential of GR-S at elevated temperatures was found to increase much more (become more negative) than that of rubber. The release of electrons (increase in negative contact-potential) and consequent disruption of electrostatic attractive forces within the material at elevated temperature probably partly accounts for the much greater decrease in tensile strength of GR-S over rubber, and is further confirmation of the electrostatic contact potential theory of reinforcement.

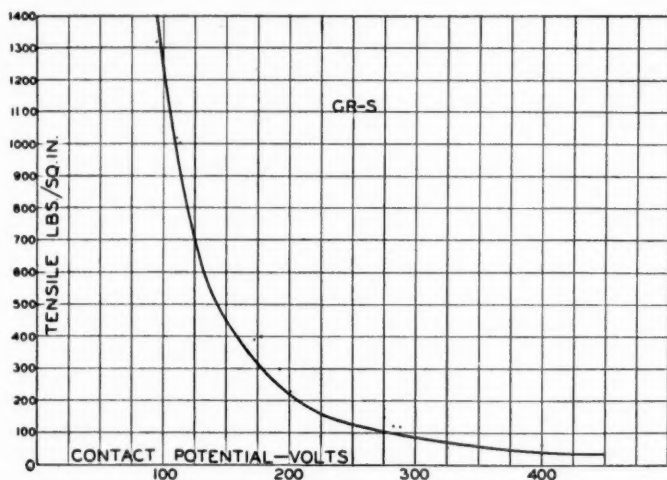


FIG. 11.—Contact potential vs. tensile strength for all GR-S compounds.

By the further application of this theory, highly positive materials, such as certain proteins, finely divided silica, and sodium silicate, which retain their positive charges at elevated temperatures and make the stocks more positive, have been found to more than double the hot tensile strengths of compounds made from GR-S latex and highly loaded with zinc oxide.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Havenhill, O'Brien and Rankin, *J. Applied Physics* **15**, 731 (1944).
- ² Havenhill and Rankin, *India Rubber World* **107**, 365 (1943).
- ³ A.S.T.M. Standards, 1941 Supplement, Part III, D15-41, p. 64.
- ⁴ Test Method Card No. 66, File S-2; dated October 23, 1943. Research Compounding Section, Research and Development Division, Office of Rubber Director, Washington, D. C.

USE AND MISUSE OF ACCELERATED AGING TESTS *

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INTRODUCTION

Most routine and research work on aging is rendered valueless by lack of appreciation of the factors responsible for different types of breakdown. The confusion is accentuated by the fact that accelerated aging tests can be used for several distinct purposes, and it is necessary to discuss these before considering aging in detail.

PURPOSES OF ACCELERATED AGING TESTS

Aging tests can be used in certain special ways or as accelerated tests of aging in service.

SPECIAL APPLICATIONS.—These are as service tests and in factory standardization. Since these do not require an acceleration of natural aging, the test can be used without prior knowledge of the type of breakdown which takes place in use, and there is no restriction concerning the type of compound tested. The physical property measured should be one which changes considerably in the course of the test.

Service Tests.—If the operating conditions are accurately known and are similar to those in one of the accelerated aging tests, the latter can be used as a service test. The physical properties should be measured under the actual conditions of aging. For example, if service is in air at 70° C, the tensile strength or other properties should be measured at 70° C, after aging in the oven at that temperature. Here the type of breakdown in the aging test is automatically the same as in service, and the results of the test are a direct measure of endurance. This use of accelerated aging tests is, however, very restricted, for each test can only simulate the conditions of one or two special applications.

Factory Standardization.—An accelerated aging test, like any other test, can be used to ensure that the output of a factory is standard. However, if the predominant type of breakdown in service is not known, the results are merely an arbitrary criterion of standard output, for the differences do not necessarily indicate a change in durability. This use of aging tests is cumbersome, since a time lag is introduced, and the test is more laborious than direct measurements, without aging, of simple properties such as tensile strength. A good example of this type of use is the TG.25A specification, where one oven aging test is used for the whole range of compounds. Yet the rubbers of different hardnesses were being produced for diverse applications by different Government departments. If an appropriate aging test had been chosen for each type of application, the results might have been some guide to durability.

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NORMAL USE.—The most obvious limitation to the use of accelerated aging tests as a guide to natural aging is that the main cause of failure in service must be known. For example, if GR-S compounds fail from atmospheric cracking in a certain application, tests in the oven or the bomb give no indication of their endurance.

Main Cause of Failure in Service.—Tests in actual service may be the only certain way of deciding this, but where the conditions of operation are known, it is possible to use a service test for the purpose. In fact, if performance is under variable conditions, a service test under repeatable conditions may be essential.

It may be possible to decide from experience the most likely cause of failure. To do this, it is necessary to take into account the breakdown to which a given rubber or compound is most susceptible, the types of failure accentuated under given conditions, and the physical properties most seriously affected by a given type of breakdown.

For example, if the service requirements demand that Butyl rubber be used for its high resistance to chemicals, and high temperatures are involved, it must be remembered that this rubber is susceptible to reversion, which is favored at temperatures of 100° C or over. The chief result of reversion is loss of modulus, which is therefore the most likely cause of failure.

Accelerated Aging Tests as a Guide to Service Life.—Having decided the main cause of failure in service, an accelerated aging test which accentuates that type of breakdown can be chosen and used in a restricted field as a guide to durability. The chief limitations are that (1) the results are only comparable when using the same basic compound, and (2) even with the same basic compound, an accurate prediction of service life is not usually possible, although a change in the accelerated aging life means a similar change in endurance.

Within these limits, accelerated aging tests can be used in factory or laboratory development work to assess improvements in durability which result from small changes in the compound, or in factory control to ensure a product of standard life.

The importance of restriction (1) above is easy to see. For example, in developing compounds containing GR-S to give improved resistance to atmospheric cracking, the exposure of stretched samples to ozone might be used as an accelerated aging test, and an increase in the ozone resistance should mean an increase in the resistance to atmospheric cracking. But if the resistance to atmospheric cracking is vastly improved, or a big change is made to the compound, or the rubber is changed *e.g.*, to Neoprene, failure may no longer be due to atmospheric cracking, and exposure to ozone will not be a guide to endurance.

TYPES OF AGING

It is essential to distinguish clearly between the various types of change which may occur as a result of aging.

Purely physical changes, such as partial freezing, which causes a hardening easily reversible by heat or work, can occur when rubber is stored at room temperature. However, this paper will be limited to permanent effects, produced by chemical changes, of which there are three main types. First, there are shallow surface changes which have a negligible effect on the mechanical properties of thick articles; secondly, deep surface changes which may

cause the failure of fairly thick articles; and thirdly, changes which occur uniformly throughout the rubber.

The types of aging are classified in Table 1.

TABLE 1
CLASSIFICATION OF TYPES OF BREAKDOWN

Effect	Mechanism	Favorable aging conditions	Rubbers particularly susceptible
<i>Shallow Surface Changes</i>			
Skin formation and crazing	Attack by oxygen or possibly vulcanization catalyzed by light	Exposure to light	Most rubbers
Discoloration			
Frosting	Ozone + moisture	Unstretched samples in humid ozonized air	
Chalking	Any surface breakdown	Depends on the particular cause	
<i>Deep Surface Changes</i>			
Atmospheric cracking	Attack by atmospheric oxidizing agents such as ozone	Exposure of stretched samples to outdoor atmosphere or ozone, shaded from direct light	Natural rubber, GR-S, Perbunan
Surface hardening or softening	Surface oxidation at high temperatures	Oxygen bomb, and particularly oven aging at 70° C or above	All rubbers
<i>Changes throughout the rubber</i>			
Loss of strength	Uniform oxidation	Aging at room temperature	Natural rubber, GR-S, Perbunan
Hardening	Probably oxidation, but may be continued cure or polymerization	Oven or bomb aging	Natural rubber, GR-S, Perbunan Butyl
Softening			

In general, several of the above effects occur simultaneously, and may interact with one another.

THE CHOICE OF ACCELERATED AGING TEST

Each type of aging will now be discussed to show the appropriate accelerated test and to indicate the directions in which improvement could be made to the present tests.

SHALLOW SURFACE EFFECTS.—Except in proofings and other thin sheets, with which we are not concerned in this paper, these changes generally affect little more than the appearance of an article.

Skin Formation and Crazing.—The formation of an inelastic skin by light in the presence of oxygen was distinguished from atmospheric cracking and mass oxidation by Williams¹, and it is by means of this skin that light can retard atmospheric cracking².

It occurs particularly in white mixes, especially those containing magnesium carbonate³, and is retarded when a small amount of black is added to absorb light⁴.

An effect reported by Morgan and Naunton⁵ may be connected with the formation of this skin. They found that the rate of absorption of oxygen by rubber in the dark, and the rate of loss of tensile strength in the bomb, were increased by preexposure to light, the increased rate of absorption continuing, after exposure for at least 24 hours, at room temperature. This oxidation, and Williams' inelastic skin, occur under similar conditions and may, therefore, be parts of the same process. If so, the formation of skin should continue in the dark after exposure to light.

Crazing is caused by the action of light in the presence of oxygen on unstretched or stretched rubber³, resulting in small cracks running in all directions to form a network. It is commonly confused with atmospheric cracking, which does not require light and where the cracks are perpendicular to the direction of stress. Crazing occurs not in the rubber but in a resinous skin⁶, and the depth of crazing is limited by the thickness of the skin. Unless the contrary is proved, it can safely be assumed that the resinous skin in which crazing occurs is identical with Williams' inelastic skin and that the crazing of this skin is merely a further stage in its breakdown.

The rate at which the skin thickens and crazing deepens becomes steadily smaller, as the underlying rubber is protected against light by the skin itself. These effects, therefore, are generally confined to a fairly thin surface layer in nonblack compounds, and are negligible in black articles. The use of light to accelerate them will be discussed later.

Discoloration.—Exposure to light and ultraviolet light can cause surface discoloration, which has been produced in vulcanized rubber by exposure either before or after cure⁷. Even in black mixes, where the light penetration is small, a bronzing can be developed. When using artificial light to evaluate discoloration, the limitations of ultraviolet light tests (see later) should be remembered.

Frosting.—In frosting, a shiny rubber surface is dulled by a maze of minute cracks, and pigment particles are exposed. This occurs when ozone attacks unstretched samples in a moist atmosphere, according to Tuley⁸, who describes an accelerated test. Frosting should not be confused with bloom, which can be removed by solvents or acid.

Chalking.—This is a loosening of surface pigment, caused by some kind of breakdown of the surface skin of rubber which normally surrounds the pigment particles. Whenever chalking occurs the kind of breakdown responsible should be traced, and an appropriate aging test used.

The mechanism of light-stimulated changes is not very clear, for vulcanization or oxygen vulcanization may occur as well as oxidative breakdown, and the effect of exposure is not necessarily immediate. However, the best accelerated test for these effects is the exposure of unstressed nonblack samples to visual light with the precautions described below.

The misuse of ultraviolet light tests is common. It cannot be too strongly emphasized that ultraviolet lamps should not be used in accelerated tests for atmospheric cracking (misnamed sun-checking), which requires the attack of an oxidizing agent (other than oxygen) on a stretched sample and is actually retarded by light.

When using light to evaluate skin formation, crazing or discoloration, it is essential to eliminate extraneous effects, especially that of ozone. The presence of ozone near discharge lamps is well known, and no doubt explains the increase in deterioration under a quartz-mercury lamp when ventilation is reduced⁹. In this respect an enclosed arc lamp is an improvement on discharge lamps for light tests and since there is no evidence that stretch accelerates any of the

light-catalyzed effects, the possibility of ozone cracking should be further diminished by exposing samples unstressed.

Another disadvantage of discharge lamps is that their radiation is confined to narrow bands of wave length instead of being spread over the spectrum as in sunlight. Before ultraviolet lamps can be used safely in accelerated sunlight tests, fundamental research on the effect of different wave lengths of monochromatic radiation is required. It is possible that the extreme chemical activity of the short-wave radiation produced in great quantity by ultraviolet lamps may cause reactions which do not occur appreciably in sunlight. Until more is known of the effect of different wave lengths, the spectral distribution of the artificial radiation should approximate closely to that of sunlight, and it is best to use thermal radiation with suitable filters. In short, the light used should be mainly visible rather than ultraviolet.

Given a standard spectral distribution, the total intensity should be measured. Radiation of too great an intensity should be avoided in view of the possibility of overheating the samples, especially as the temperature of samples is seldom rigidly controlled. With high intensities of radiation, the rate of oxidation may be limited not only by the rate of light-activation, but by the rate of diffusion of oxygen (q.v. a similar effect in high temperature oven-aging). If this factor operates, the result is no longer proportional to the amount of radiation.

There is little point in testing the light resistance of stocks containing black, which prevents any appreciable penetration by light. Physical differences in light resistance, depending on color, should not be confused with chemical differences, e.g., between synthetic rubbers in mixes of the same color and transparency.

The difficulty of estimating the extent of skin formation by visual methods may explain the American preference for measuring loss of tensile strength and elongation at break during light-aging. If, as suggested, skin formation may continue in the dark after exposure to light, the preferred method of estimation should be applied only after the sample has been rested for a few days in the dark to allow the completion of the light-stimulated reactions.

The foregoing considerations may explain the discrepancies reported by Ingmanson¹⁰, between the results from ten different laboratories in the U. S. The apparatus used differed in small details but consisted of "weatherometers" and, although the relative orders of five compounds agreed in most cases, the degree of deterioration varied from one laboratory to another. Nevertheless, a useful suggestion resulting from this work was that a single compound should be chosen for detailed study to establish uniformity between the different test units. No matter what accelerated test is being used, this approach to the problem is sound and essential if discrepancies between different laboratories are to be understood and removed. If such a coöperative program were to be undertaken in this country as one result of this conference, it would be well worth while.

DEEP SURFACE CHANGES.—There are two types of aging which, although not occurring uniformly throughout thick articles, can affect the surface to a considerable depth, namely, atmospheric cracking, and surface hardening or softening. Though essentially surface effects, they are generally more serious than those already discussed.

Atmospheric Cracking.—The misconception that light is necessary for atmospheric cracking has been perpetuated in the name "sun-checking". It has

been strengthened by confusion with crazing, which requires light, and also by the fact that atmospheric cracking does not occur appreciably indoors, owing not to absence of sunlight but to dissipation, by contact with indoor surfaces, of the active agents present in outdoor air.

The critical elongation of 10 to 20 per cent at which atmospheric cracks reach maximum size is explained by the dependence of the rates of crack formation and growth on elongation². A similar effect is found with ozone cracks, which has suggested that ozone alone is responsible for atmospheric cracking. Ozone is certainly a major factor, but may not be the only one, for the atmosphere contains nitrogen tetroxide as well as ozone¹¹, and it is possible that other

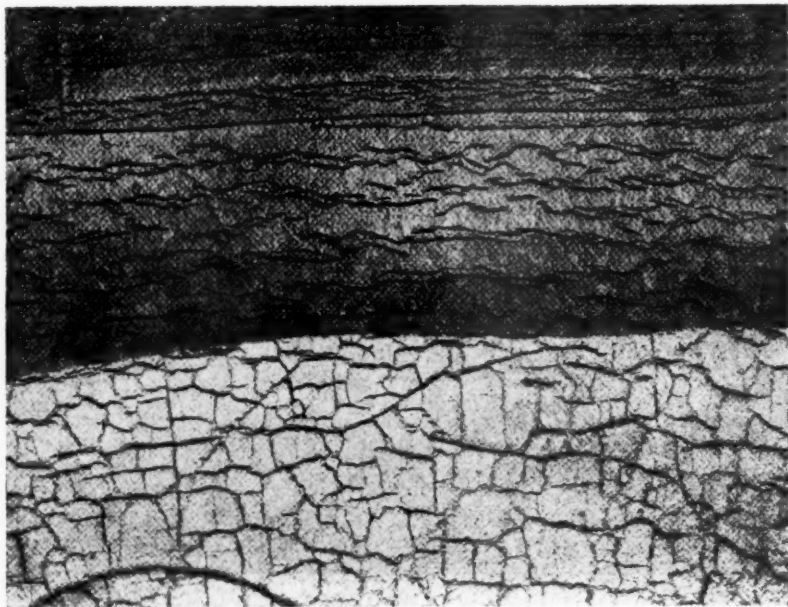


FIG. 1

atmospheric oxidizing agents may act in a similar way. For all practical purposes, however, ozone may be considered to be the cause of atmospheric cracking.

Differences in the appearance of atmospheric cracking and crazing are illustrated in the sidewall of an enemy airplane tire (Figures 1 and 2). Under the same service and exposure conditions, atmospheric cracking and crazing have occurred side by side, sharply separated by the junction line of the two compounds.

In the black portion of the sample shown in Figure 1 the atmospheric cracks are roughly parallel and lie perpendicular to the stress in the sidewall, whereas in the white portion the crazing is in all directions, forming a network. Examination of the sample shows that the surface of the white compound has hardened into a shallow skin (Williams' inelastic skin) in which the crazing appears, whereas in the black portion no surface hardening can be

detected. Figure 2 shows that atmospheric cracking is more serious, since the cracks have penetrated to an appreciable depth, but the depth of crazing is inappreciable. The cracks in the black compound are unlikely to be flex-cracks since there is relatively little flexing in an airplane tire, and flex-cracks would not cease abruptly at the junction of the white and black portions.

Although the composition of the white and black compounds is not known, their color is sufficient to explain this effect. Skin formation and crazing did not occur in the black portion because they require light, and this is absorbed by the carbon black. Atmospheric cracking did not occur in the white portion because Williams' inelastic skin was formed on the surface by the action of light in the presence of oxygen, and prevented the access of ozone or other oxidizing agents which produce atmospheric cracking.

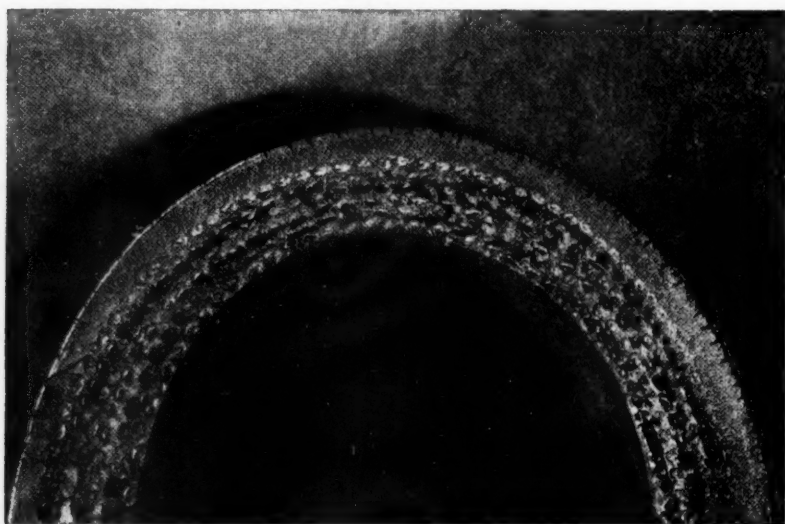


FIG. 2

When atmospheric and ozone cracking are distinguished from skin formation and crazing, many otherwise contradictory results become clear. Werkenthin, Richardson, Thornley and Morris¹², reported the following anomalies:

- (1) A stretched sheet of highly thermoplastic rubber caulking compound, in comparison with high-grade pure rubber compounds, showed remarkable resistance to accelerated ultraviolet light aging and to sunlight aging.
- (2) A white stock of a certain synthetic rubber had several times the light resistance of a black stock.
- (3) Another synthetic had good resistance to ozone and yet poor resistance to sunlight and ultraviolet light.

Ozone, besides being present in the sunlight tests, was probably also present in the ultraviolet light tests, so that atmospheric cracking could occur in the stretched samples in both. The results are easily explained:

- (1) A caulking compound of high stress decay, when exposed at constant strain, would quickly become stress-free and thus resist atmospheric or ozone cracking better than high-grade rubber compounds. In fact, compounding for high permanent set is a well-known method of obtaining ozone resistance in cables.
- (2) The cause of breakdown was probably atmospheric cracking, which is less serious in white mixes through the formation by light of an oxidized skin which protects the rubber against ozone.
- (3) There is no reason why a rubber should not have good resistance to ozone or atmospheric cracking and yet poor resistance to skin formation and crazing, especially if compounded in a transparent or white stock of high stress decay.

Although it is not absolutely certain that ozone is the only oxidizing agent responsible for atmospheric cracking, at present the only possible accelerated test is the exposure of stretched samples to ozone. To ensure that only atmospheric cracking can occur in the test, skin formation and crazing should be reduced by exposing the samples to ozone in the dark. When outdoor exposure is used to evaluate this effect, the stretched samples should be shielded from direct light for the same reason. Compounds to be evaluated by exposure to ozone or the atmosphere should, if not already black, contain a small percentage of added black to minimize the effects of incidental exposure to light.

Although samples must be under stress during atmospheric cracking tests, there is little agreement as to the best amount of surface stretch, and in estimating the extent of cracking it is not clear whether it is best to use visual grading methods³ or measurements of physical properties. If physical tests are used they must be sensitive to cracks; suitable tests are those which have been used to measure flex-cracking, *e.g.*, tensile strength¹³ or bending moment¹⁴. Since the amount of ozone required to produce cracks in stretched rubber is small, the formation of a skin is inappreciable, and changes in the physical and chemical properties of the bulk of the rubber cannot be detected until the ozone has been acting for a much longer time than is required to produce cracks. Tests such as hardness or resilience cannot therefore be used to assess atmospheric or ozone cracking.

Surface Hardening or Softening.—These effects are prominent in accelerated aging tests at elevated temperatures, and although they occur by accident rather than by design in these tests, the discussion in this section has been broadened to include the general advantages and disadvantages of oven and bomb aging tests. These were originally intended as general aging tests, but since the advent of antioxidants and age-resistant synthetic rubbers, other kinds of deterioration such as those due to light and ozone have come into prominence and cannot be assessed by tests in ovens or bombs. If free from the disadvantages discussed here, oven and bomb tests could at best accelerate only the type of degradation which takes place indoors in absence of light, as in drawer or shelf aging, but they can be no guide to natural aging in the presence of either light, or ozone when the samples are stretched.

Oxidation occurs only in the outer layer of samples aged at high temperatures, causing surface hardening with most vulcanized rubbers and surface softening with unvulcanized rubbers. In air at 80° C and above, the absorption of oxygen by vulcanized natural rubber⁵ is so rapid in relation to the rate of diffusion of oxygen that it can penetrate only to a small depth before being

absorbed, and the center of the sample may be devoid of oxygen. The depth of the outer layer is practically constant throughout the period of aging, for the physical properties are destroyed long before the absorption ceases. This depth is increased by antioxidants, which reduce the rate of absorption, and decreased by heat, which increases the rate of absorption more than the rate of diffusion. Rubber aged in an oven or oxygen bomb is not, therefore, homogeneous throughout.

Figures 3 and 4 illustrate this clearly. Figure 3 shows the broken end of a tensile ring after aging in the oven at 150° C, and is typical of all rubbers after aging at this temperature. A hard outer skin surrounds the softer inner core.



FIG. 3

Even Butyl rubber, which is relatively resistant to oxidation, had a similar appearance, but the outer skin did not appear to be harder than the core, and might even be softer.

It is difficult to interpret the results of tests made on samples which are heterogeneous after aging at high temperatures, since the physical tests for rubber have been designed for homogeneous samples. To improve tensile strength results with these samples, it has been suggested that the calculation should be based on the area of cross-section of the center portion, which would double the figure obtained with the sample shown in Figure 3. One objection to this is that the core has been heat-aged in the comparative absence of oxygen, and could hardly be expected to give results correlating with oxidation at room

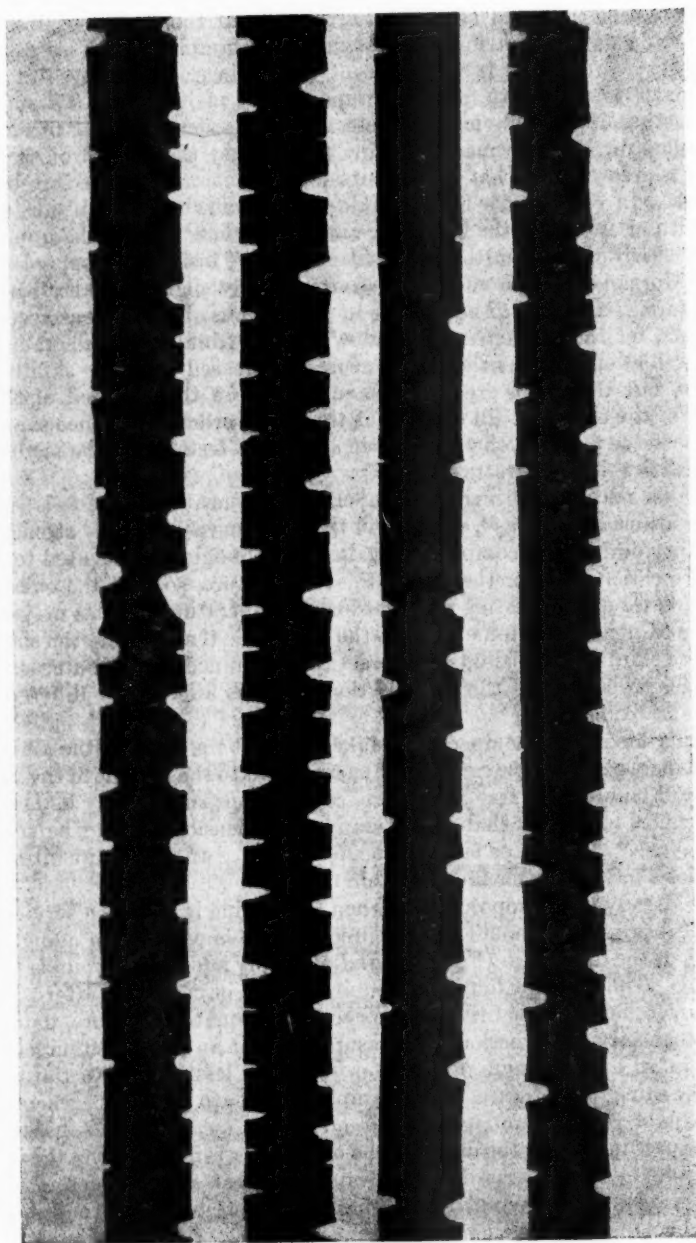


FIG. 4

temperature. A further difficulty is seen from Figure 4 showing tensile rings which have been stretched 17 per cent after aging at 150° C. The stresses and strains are not evenly distributed throughout the samples, which are analogous to multiple Van Wijk tear test-pieces. These rings are hardly suitable for measuring tensile strength, and the impossibility of removing the outer skin before testing is also obvious. These surface-hardened rings, incidentally, when pulled on a tensile machine show clearly that the stretch on the inside of a ring is greater than that on the outside, for the cracks in the skin begin on the inside. In Figure 4 the lower visible side of each ring is the inside, and the total width of cracks on the lower edge is greater than that on the upper edge, showing clearly that when the ring is stretched the inside is elongated most.

The Morgan-Naunton effect, which occurs only slightly if at all at room temperature, is a serious disadvantage in using ovens and bombs as accelerated aging tests, for the accelerated breakdown differs from normal degradation in type as well as speed. As the temperature is increased the outer skin becomes shallower, but there is a greater difference between the material of the skin and that of the core after an equivalent time. In order to produce samples as homogeneous as possible, therefore, oven and bomb tests should be made at the lowest practicable temperature.

A further reason for using low temperatures in heat-aging tests is supplied by observations of Le Bras¹⁵, who found that the curves of tensile strength and oxidizability of different compounds against time of aging at elevated temperatures were closer together the higher the temperature, so that the oven aging test has greater discriminating power at lower temperatures. This may well be due to the Morgan-Naunton effect, for the higher the temperature the shallower the surface skin, and as oxidation is practically confined to this outer skin, the smaller the proportion of the cross-section which is affected by differences in resistance to oxidation.

As oxidation at high temperatures takes place at the surface, the amount of oxidation increases with the ratio of the surface area to the volume of the sample. In oven and bomb aging tests, therefore, comparisons should only be made between samples of similar shape, and standard dimensions should be specified for general use. This shape factor also affects service at high temperatures, for thick articles have a longer life than thin ones.

It has already been proposed that when oven-aging is used as a service test, the physical properties should be measured at the temperature of aging. The properties of the outer skin (Figures 3 and 4) supply additional grounds for this suggestion. The skin was found to be quite flexible immediately after removal from the oven, but became brittle when cooled to room temperature, indicating that heterogeneity is less serious in measurements at an elevated temperature.

Tests in an oxygen bomb, apart from requiring less time than those in an oven at the same temperature, giving samples which are less heterogeneous at a given stage of degradation. Although no direct measurements have been made, it is presumed that the depth of the outer layer is increased by the oxygen pressure. Reduction of the Morgan-Naunton effect may, therefore, be an additional reason for the popularity of the bomb aging test in spite of its being more cumbersome than oven aging tests.

Another disadvantage of oven and bomb tests as used at present is that volatile antioxidants may be lost from protected mixes and contaminate the unprotected control samples, so that the apparent age resistance of protected mixes is diminished and that of control samples increased. This effect is not

likely to occur in service, and should be reduced by using low temperatures in accelerated aging tests. To reduce contamination further the procedure of aging samples in individual containers should be more widely adopted. In the oven, the container would have to prevent loss of antioxidant, and yet allow access of oxygen without becoming filled with an accumulation of nitrogen from the incoming air. One way of doing this would be to have a small hole in the container, fill it with oxygen at room temperature, and age in an oven filled with oxygen at atmospheric pressure.

CHANGES THROUGHOUT THE RUBBER.—Apart from the surface effects already discussed, the rubber can change uniformly throughout, with surface changes superimposed. As the chemical basis of these changes is not yet clear, they have been divided according to the main physical result.

Loss of Strength.—The failure of unstressed natural rubber in the dark, especially in absence of antioxidants, is chiefly by loss of strength, with some hardening or softening. This occurs if articles are aged indoors, when the rubber becomes cheesy and friable. Little change occurs when vulcanized natural rubber is heated in absence of oxygen¹⁶, suggesting that oxidation plays a large part in its aging. This type of breakdown is commonly assessed by tensile strength determinations after Geer oven or oxygen bomb aging.

For the oxidation to be uniform it must be relatively slow so that oxygen can penetrate to the center of the samples without being absorbed in the outer layers. The uniformity is therefore greatest at low temperatures and with rubbers either having an intrinsic resistance to oxidation or containing antioxidants. Merely raising the temperature is an unsatisfactory method of acceleration because of the loss of uniformity. The Geer oven and oxygen bomb, which were designed to assess the effects of oxidation, operate at temperatures at which considerable nonuniformity occurs, although it is less serious in an oxygen bomb than in an oven at the same temperature after an equivalent time. The oxygen bomb at temperatures below 70° C may, therefore, be a suitable accelerated test for uniform oxidation.

Hardening or Softening.—In oven or bomb aging, especially with some synthetic rubbers, loss of strength may be a minor effect compared with hardening or softening. Hardening predominates with GR-S, Perbunan, and Neoprene, but softening can be serious with Butyl, and with natural rubber at high temperatures.

Increases in hardness which occur in oven aging tend to be accompanied by increases in resilience, and Figure 5 shows the resilience of a GR-S tread type stock under various aging conditions. The increase is greater than would be obtained by a continuation of press-cure and is not, therefore, the same effect that would be produced by heat in an enclosed space. It is tempting to attribute this to continued polymerization or cure, but if so, the increase must be facilitated by the liberation of end-products trapped in the press. Although oxidation has been shown to be the main factor in the heat aging of natural rubber, similar investigations with GR-S, though showing that oxygen has some effect, have not given conclusive results¹⁷. The apparent contradiction of these experiments may be explained by the fact that oxygen can both increase and decrease chain length, and the balance between the two types of reaction may be easily upset. With natural rubber the delicacy of this balance is well known, for in the oven aging of the same sample softening may succeed hardening or *vice versa*.

When softening predominates, the change is called reversion, as in effect the rubber tends to return to the unvulcanized state. Under appropriate condi-

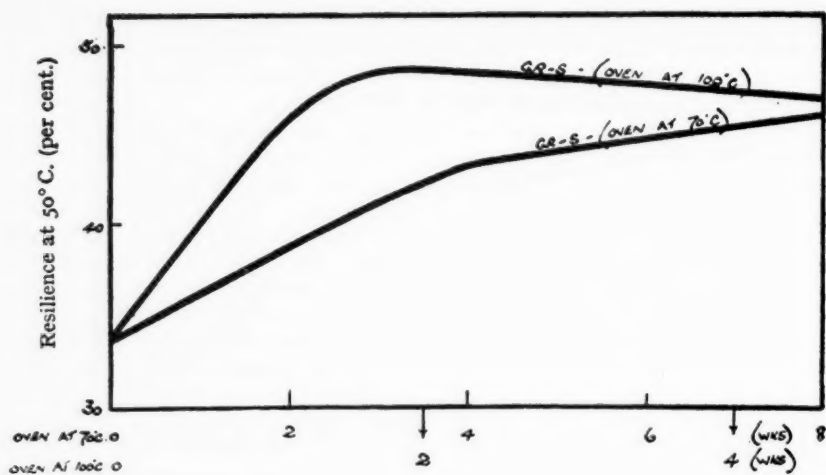


FIG. 5

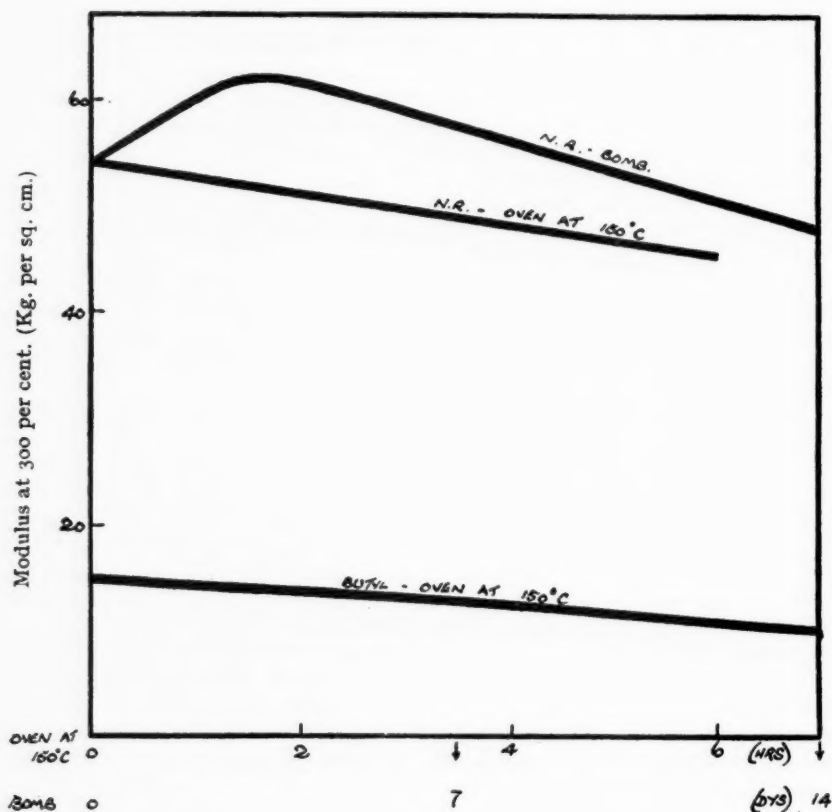


FIG. 6

tions this can occur with all rubbers, but may be reduced by the presence of excess curing agents. It may be masked by surface hardening and similar effects, and must therefore be tested by properties of the mass, such as modulus. Figure 6 shows graphs of three samples in which reversion is indicated by a fall in modulus.

CHOICE OF PHYSICAL PROPERTY TO FOLLOW OVEN OR BOMB AGING

The rate of change of a physical property is not generally constant throughout the period of aging, most properties changing rapidly at first and then more slowly. It is not, therefore, possible to quote a rate of change except over some arbitrary interval, while the use of the initial rate is exposed to considerable experimental error. Differences in shape have been ignored by most authors when estimating temperature coefficients, although accurate comparisons can only be made between curves of similar shape.

In using accelerated aging tests as a guide to service life, the physical property chosen to follow aging should change appreciably during the test, and it is necessary to take into account the extent to which the measurements are influenced by the surface effects already discussed.

When considering different physical properties, it is useful to remember the general way in which they are interrelated. Instances are the partial correlation between hardness and resilience, and the negative correlation between modulus and swelling.

The relative merits of some physical properties are discussed below.

Tensile Properties.—Accelerated aging has been followed almost exclusively in the past by means of tensile strength. Whereas this may be justified with natural rubber, it is unsatisfactory with most synthetic rubbers, as the shape of the graph of tensile strength against time of aging varies considerably according to the synthetic rubber and the aging conditions.

If a single criterion of aging is to be used, elongation at break is far superior to tensile strength. Elongation has the advantage that its graph against time of aging has an almost constant shape with different rubbers and aging conditions and is roughly exponential. Fairly straight lines are obtained when the logarithms of elongation are plotted against time of aging, and the slope of these lines provides a convenient means of comparison which is widely applicable. A further advantage of elongation is that it is sensitive both to loss of tensile strength and to increases in modulus, which in the absence of reversion are the most serious changes which occur. Before relying on elongation as a criterion of aging it is necessary to check the modulus to ensure that there is no reversion. If reversion is serious, then tensile strength is to be preferred to elongation, e.g., with Butyl at high temperatures when tensile strength decreases rapidly but elongation is maintained owing to softening.

Swelling.—As would be expected during the course of accelerated aging, volume swelling is almost inversely proportional to modulus, and when tensile strength is constant, swelling is closely related to elongation at break. Swelling measurements, therefore, give no more information than tensile properties and are more seriously affected by surface hardening. The figures are erratic, owing to variable amounts of exposed surface, the amount and type of surface cracking of the swollen sample depending on the initial surface imperfections. This is illustrated clearly in Figures 7 and 8, which show the surface of aged rubber at the same magnification, before and after swelling in benzene for 2 days at room temperature.

Hardness.—Surface properties such as hardness indicate the extent of surface hardening or softening, but with heterogeneous samples have little meaning unless the depth of the outer layer is known and the properties of the inner core assessed by a test such as modulus.

Resilience.—The accelerated aging of natural rubber can be followed by resilience, which falls fairly rapidly, but which is hardly affected in Perbunan, Neoprene-GN and Butyl rubbers. Resilience measurements are upset, not only by the heterogeneous nature of the test-piece, but also because varying amounts of the skin are removed when the sample is buffed to a standard thickness for test.

Other Physical Properties.—In view of the difficulties of interpreting the results of the simpler tests on samples after accelerated aging, there is little to be gained by measuring complex properties, such as abrasion resistance and flexing, until oven or bomb tests have been improved, or superseded by tests in which the sample remains homogeneous.

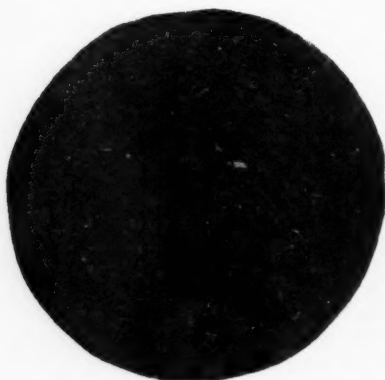


FIG. 7



FIG. 8

OTHER CRITERIA OF ACCELERATED AGING

In an attempt to avoid the drawbacks of measuring the normal physical properties to follow oven or bomb aging, other measurements have been proposed, and two of them will be discussed.

Oxidation.—This can be measured either by the amount of oxygen or oxidation products present in the rubber after aging, or by the rate of absorption of oxygen.

The first method suffers from the practical drawback that chemical analysis is required, which makes it hardly suitable for routine tests.

The second method with the latest apparatus is quick and convenient. The changes brought about by aging can be detected much sooner than by measurements of physical properties, and different types of antioxidants can be separated. For example, antioxidants which act merely as oxygen absorbers and protect rubber only for a short time, show up badly in this test by having a high rate of absorption. The results may, however, be affected by variations in the efficiency of utilization of oxygen, such as surface overutilization, due to incidental exposure to light, which produces little change in mechanical properties.

For oxidation measurements to have full practical value, it is necessary to correlate oxidation with the loss of rubberlike properties for each rubber.

Depth of the Oxidized Layer.—Morgan and Naunton⁵ have measured the depth of the oxidized layer produced by aging at elevated temperatures, and have suggested that the efficiency of antioxidants can be evaluated by this method. More attention should be given to this, for besides showing the extent of heterogeneity, the method is preferable to measuring mechanical properties, which are liable to large errors. Physical properties should be used to assess the rate of degradation at room temperatures, and then the relations between depth of penetration in the accelerated test and rate of degradation at room temperature could be established. Work on these correlations is in hand.

CONCLUSIONS

1. The general term, aging, covers many different changes. When carrying out both natural and accelerated aging tests, it is essential to distinguish clearly between these changes and to test them separately if confusion is to be avoided. The chief agents responsible for aging are light, ozone, and oxygen, with or without heat. Each one of these can cause several types of degradation, the predominant type depending on the rubber and the conditions.

2. It is important to appreciate the difference between crazing and atmospheric cracking. Crazing is caused by the action of oxygen stimulated by light, whereas atmospheric cracking is due to attack by ozone on stretched samples.

3. It is suggested that crazing is produced in Williams' inelastic skin, and that the light-catalyzed oxidation which causes these effects is the same as that studied by Morgan and Naunton.

4. The only types of aging which require light are skin formation, crazing, and discoloration, and it is misleading to use light to test other types of aging. In the present state of knowledge the routine use of ultraviolet lamps should be abandoned until further work is done on the effect of different wave lengths. Instead, an enclosed arc should be used with a spectrum as close as possible to that of sunlight. The results of many light tests have been made useless by the omission of certain obvious precautions. For example, radiation of too great an intensity should be avoided, and the samples should not be stretched.

5. It is futile trying to use ovens, bombs or ultraviolet lamps as accelerated tests for atmospheric cracking, and it is impossible to correlate these tests with outdoor aging of stretched samples. The only accelerated test, at present, is the exposure of stretched samples to ozone.

6. When evaluating atmospheric cracking, exposure to ozone should be in darkness so as to reduce skin formation and crazing; similarly, in outdoor exposure tests the stretched samples should be shielded from direct light.

7. In oven and bomb tests at high temperatures, the absorption of oxygen is so rapid in relation to the rate of diffusion that it can penetrate only to a small depth before being absorbed. Samples are, therefore, heterogeneous and there are several resulting deficiencies in the measurements of physical properties. Ovens and especially bombs, operated at lower temperatures, should give more accurate information.

8. Oxygen bomb tests, apart from requiring less time than those in an oven at the same temperature, are preferable as the samples are less heterogeneous at a given stage of degradation.

9. In oven or bomb tests, comparisons should be made only between samples of similar shape, and standard dimensions should be specified for general use.

10. When assessing the value of antioxidants, care should be taken to avoid mutual contamination by using special individual containers.

11. To follow oven or bomb aging at least two physical properties should be measured.

12. As a general criterion of aging, elongation at break, in the absence of reversion, is most suitable to follow oven or bomb aging. Modulus should be checked in case reversion occurs, and if so, tensile strength is to be preferred to elongation at break.

13. When heat aging tests are used as service tests, the physical properties should be measured at the temperature of aging.

14. To be able to coördinate results from different laboratories in this country, a detailed study of the accelerated aging of a single compound should be undertaken. Such a program requires the coöperation of all the main laboratories in this country.

REFERENCES

- ¹ Williams, *Ind. Eng. Chem.* **18**, 367 (1926).
- ² Williams, *Ind. Eng. Chem.* **18**, 367 (1926); Evans, *Trans. Inst. Rubber Ind.* **5**, 442 (1930); Van Rossem and Talen, *Kautschuk* **7**, 79, 115 (1931); Depew, *Ind. Eng. Chem.* **24**, 992 (1932).
- ³ Newton, *J. Rubber Research* **14**, 27, 41 (1945).
- ⁴ Turner, *Trans. Inst. Rubber Ind.* **10**, 21 (1934).
- ⁵ Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, 1938, p. 599.
- ⁶ Depew, *Ind. Eng. Chem.* **24**, 992 (1932); Morris, James and Werkenthin, *Rubber Age* (N. Y.) **51**, 205 (1942).
- ⁷ Defries and Naunton, *Trans. Inst. Rubber Ind.* **4**, 289 (1928).
- ⁸ Tuley, *Ind. Eng. Chem.* **31**, 714 (1939).
- ⁹ Barr, *Trans. Inst. Rubber Ind.* **5**, 31 (1929); Wurm, *Kautschuk* **8**, 21 (1932).
- ¹⁰ Ingmanson, Am. Soc. Testing Materials, 45th Annual Meeting, *Comm. Report and Tech. Papers* **42**, 392 (1942).
- ¹¹ Edgar and Paneth, *J. Chem. Soc.*, **1941**, p. 511, 514.
- ¹² Werkenthin, Richardson, Thornley and Morris, *Rubber Age* (N. Y.) **5**, 199 (1941); *India Rubber World* **105**, 264 (1941).
- ¹³ Cooper, *Ind. Eng. Chem. Anal. Ed.* **2**, 391 (1930).
- ¹⁴ Rainier and Gerke, *Ind. Eng. Chem. Anal. Ed.* **7**, 368 (1935).
- ¹⁵ Le Bras, *Rev. gén. caoutchouc* **21**, 3 (1944).
- ¹⁶ Jones, *Ind. Eng. Chem.* **17**, 871 (1925); Kohman, *J. Phys. Chem.* **33**, 226 (1929); Reed, *Ind. Eng. Chem.* **21**, 316 (1929).
- ¹⁷ Sturgis, Baum and Vincent, *Ind. Eng. Chem.* **36**, 348 (1944); Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944).

METHODS OF CALCULATING AND REPRESENTING RHEOLOGICAL PROPERTIES, USING DATA FROM THE PARALLEL-PLATE PLASTOMETER *

J. R. SCOTT

INTRODUCTION

Theoretical investigations of the parallel-plate plastometer¹ have shown how certain fundamental rheological constants may be deduced from the readings obtained. The methods there described, however, were too involved for normal laboratory use, and so have not been extensively applied. As the study of plastic flow will play an important part in future research work on rubberlike materials, it becomes desirable to have some procedure whereby the purely empirical plastometer readings can be used to obtain, if only approximately, the fundamental relation between stress and rate of flow. The object of this note is to present one method that has been worked out for this purpose. It must be noted (1) that this method is tentative, since there has not yet been time to try it out thoroughly, and (2) that the method applies only to pseudoviscous materials, *i.e.*, those obeying Equation (1) below, and such that the rate of shear under a constant shear stress does not vary with period of time. It is hoped, however, that by presenting the method at this stage, those concerned with the study and measurement of plasticity will be enabled to apply it and so gain experience as to its value.

GENERAL CONSIDERATION OF THE PROBLEM

Symbols used: R = rate of shear, per second
 S = shearing stress (megadynes per sq. cm.)
 c = consistency (reciprocal of Bingham's "mobility")
 n = positive numerical constant
 V = volume of specimen (cc.)
 θ_0 = initial height of specimen (cm.)
 θ = height of specimen after compression (cm.)
 t = time of compression (seconds)
 P = compressive force (megadynes)

(Note that all quantities here and throughout the report are expressed in c.g.s. units.)

The rheological properties of a pseudoviscous material, *i.e.*, one obeying the relation:

$$R = (S/c)^n \quad (1)$$

can be defined in terms of c and n . Of these, n , being a pure number, is independent of the units used and therefore has an absolute significance. On the other hand, c is the shear stress required to produce unit shear rate; since the

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latter involves time, the value of c depends on the units in which time is expressed, and (since n varies) the relative c values for different materials will vary according to the time unit chosen. To this extent c is an unsatisfactory means of expressing rheological properties.

The best means at present available is a graph of shear rate against stress, preferably on logarithmic scales so as to give a straight line, and covering the range of stress values actually obtained in the parallel-plate test. It thus becomes desirable to have a simple procedure for deriving such a graph from the readings obtained in the test. The object of this report is to describe suitable methods.

It will be assumed that logarithmic scales are to be adopted, so the problem is to find the easiest way of deducing the relation between $\log S$ and $\log R$.

PROCEDURE USING QUICK METHOD OF DETERMINING n

METHOD OF DETERMINING n

This is derived from Equation (7) of Part I² of the series on parallel-plate plastometry. In connection with this equation it must be noted that in normal practice K , which is actually $\theta_0 - \frac{1}{2}(5n + 3)$, is so much smaller than $\theta - \frac{1}{2}(5n + 3)$ that it can be neglected without appreciably affecting the deduced value of n . From this equation it follows that if θ_1 and θ_2 are the heights after compression periods t_1 and t_2 then:

$$n = \frac{0.4 \log (t_2/t_1)}{\log (\theta_1/\theta_2)} - 0.6 \quad (2)$$

(Note all logs in this note are to the base 10.)

It is convenient to take $t_2 = 10t_1$ so that $\log (t_2/t_1)$ becomes unity.

In practice several values of n are obtained using various pairs of compression periods, *e.g.*, $\frac{1}{2}$ and 5 minutes; 1 and 10 minutes; 2 and 20 minutes; 3 and 30 minutes, etc. If the material is truly pseudoviscous, according to Equation (1), and provided errors due to the sources noted below are negligible, all these values of n will be equal. As these errors affect chiefly the readings at very short compression periods (say, less than 1 minute), the n values obtained by using such readings may be unreliable. If the value of n is found to increase progressively as the compression periods are lengthened, this probably means that the material shows a "yield value" (limiting stress below which no flow occurs) and so does not follow Equation (1); in such cases true n values cannot be deduced by the method here described.

The sources of error referred to above are: (1) Since the method depends directly on t , it requires the beginning of the compression to be timed exactly—not always an easy matter; an error dt in timing the start produces an error (dn) in n equal to approximately:

$$\frac{0.43dt(t_1 - t_2)(n + 0.6)}{t_1 t_2 \log (t_2/t_1)}$$

e.g., with $t_2 = 10t_1$, $dt = 0.1t_1$, and $n = 5$, dn equals -0.22 ; (2) The method assumes that the behavior of the specimen during the early stages of compression is represented by Equation (7) of Part I², which is probably only very approximately true.

CONSTRUCTION OF LOG $S/\log R$ GRAPH

Having determined n , the graph can be obtained from any reading of height (θ) at a given compression time (t). From Equation (1) above and Equation (7) of Part I² it follows that:

$$\log R = n \log S - \frac{1}{2}(5n + 3) \log \theta - \log t - M \quad (3)$$

where

$$M = \log \left[\frac{(5n + 3)(3n + 1)^n \pi^{\frac{1}{2}(n+1)} P^n}{2^{n+1} n^n (n + 2) V^{\frac{1}{2}(3n+1)}} \right]$$

It is convenient to put $S = 0.1$ megadyne per sq. cm., since this is of the order of the stresses actually obtained in the parallel-plate plastometer (note that 1 megadyne is very nearly the weight of a 1 kg. mass). Hence (3) can be written:

$$\log R_{0.1} = -[n + \frac{1}{2}(5n + 3) \log \theta + \log t + M] \quad (4)$$

Since P is normally standardized at 5 kgm. (equivalent to 4.903 megadynes) and V is either 1 or 2 cc., the values of M corresponding to various values of n can be tabulated or graphed (see Figure 1).

In using Equation (4) it is important to note that θ and t must be expressed in cm. and seconds, respectively.

The required log $S/\log R$ graph (log S being the abscissa and log R the ordinate) is obtained by drawing a straight line of slope n through the point $(-1, \log R_{0.1})$. The appropriate range of S values over which the graph should extend, i.e., the maximum and minimum stresses in the parallel-plate test, is determined by the method described in the section below on the Calculation of Shear Stress in Specimens.

PROCEDURE USING ACCURATE METHOD OF DETERMINING n DETERMINATION OF n

This is carried out by plotting values of $\log (d\theta/dt)$ as ordinate against $\log \theta$ as abscissa, the slope of the resulting straight line being equal³ to $\frac{1}{2}(5n + 5)$.

CONSTRUCTION OF LOG $S/\log R$ GRAPH

This can be carried out as described above in the section on the Construction of Log $S/\log R$ Graph, but this procedure has the disadvantage that it depends on a single reading of θ , and so is less accurate than the following, which makes better use of the data available.

From the smoothed graph of $\log (d\theta/dt)$ against $\log \theta$ a value of $\log (d\theta/dt)$ is read off at any convenient value of $\log \theta$, preferably near the middle of the graph. The values are substituted in the following equation (derived from Equation (1) above and Equation (6) of Part I²).

$$\log R_{0.1} = -n - \frac{1}{2}(5n + 5) \log \theta + \log (d\theta/dt) - N \quad (5)$$

where

$$N = \log \left[\frac{(3n + 1)^n \pi^{\frac{1}{2}(n+1)} P^n}{2^n n^n (n + 2) V^{\frac{1}{2}(3n+1)}} \right]$$

(Note that, since $\frac{1}{2}(5n + 5)$ is the slope of the $\log (d\theta/dt) - \log \theta$ graph, its value is already known.)

Values of N , for $P = 4.903$ megadynes (5 kg.) and $V = 1$ or 2 cc., are given in Figure 1. In using Equation (5), θ must be expressed in cm. and $d\theta/dt$ in cm. per sec. From n and $\log R_{0.1}$ the $\log S/\log R$ graph is constructed as described above, in the section on the Construction of $\log S/\log R$ Graph.

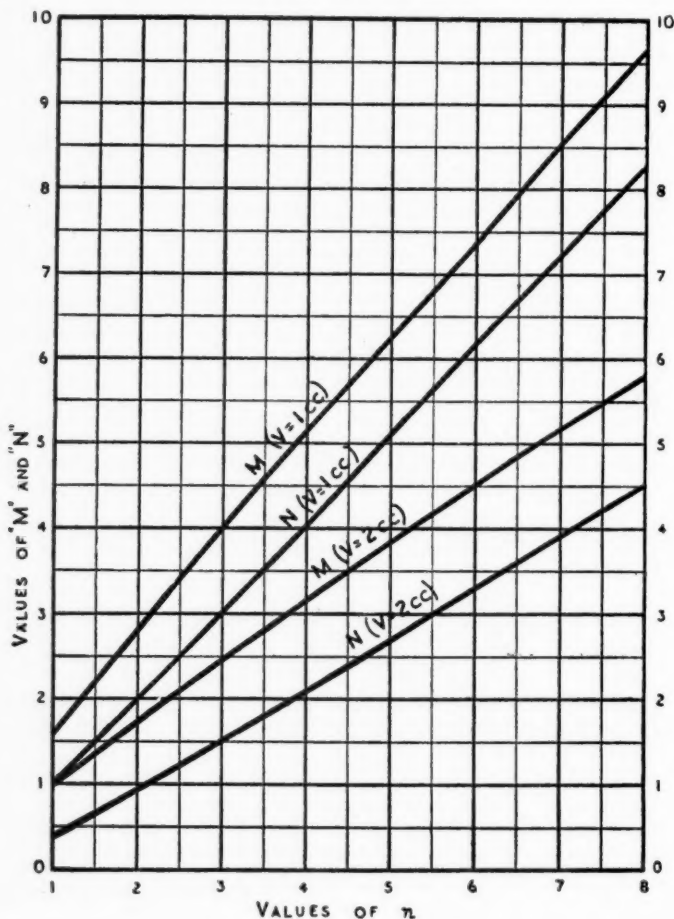


FIG. 1.—Graphs of M and N against n .

CALCULATION OF SHEAR STRESS IN SPECIMENS

As the stress varies from point to point, in the specimen, only the mean value will be considered here. An approximate formula, deduced from the results of Part I², is:

$$\text{mean shear stress } (\bar{S}) = \frac{0.9(3n + 1)P\theta^{5/2}}{(2n + 1)V^{3/2}} \quad (6)$$

Since an exact value is not required for the present purpose, and the quantity $(3n + 1)/(2n + 1)$ varies only between 1.33 (when $n = 1$) and 1.5 ($n = \infty$),

it is sufficient to use the simplified "average" formula:

$$\bar{S} = 1.25P\theta^{1/2}/V^{3/2} \quad (7)$$

Values of $\log \bar{S}$, for $P = 4.903$ megadynes (5 kg.), are shown in Figure 2.

In drawing the $\log S/\log R$ graph it is reasonable to take the mean stresses corresponding to the first and last, i.e., maximum and minimum, thickness readings in the parallel-plate test, and to draw the graph only between these stress limits, since any extension above or below these limits represents an extrapolation which may not be justified.

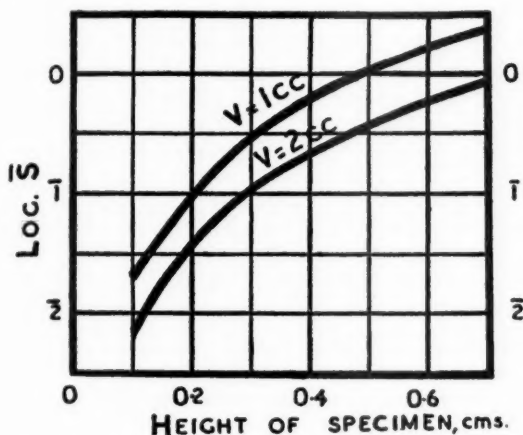


FIG. 2.—Relation of mean stress (S) to height of specimen (θ).

SUMMARY

A tentative method is described for obtaining, from readings of the parallel-plate Williams plastometer, the fundamental flow relation of the material under test, and for representing this relation graphically in a manner that facilitates comparisons between different materials.

REFERENCES

- ¹ Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931); **10**, 481 (1935); *RUBBER CHEM. TECH.* **8**, 587 (1935).
- ² Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931).
- ³ Scott, *Trans. Inst. Rubber Ind.* **7**, 177 (1931).

CAPACITY OF RUBBER MIXTURES TO BE MOULDED *

ROGER A. HUBLIN

In the plastics industry, an estimation of the behavior of its raw materials when milled is regarded as a precautionary measure of the greatest importance. Apparatus, in some cases of a very refined type, has been utilized to study the influence of various factors, such as temperature, pressure, time, etc. In contrast to this, in the rubber industry there have, to our knowledge, been extremely few systematic investigations in this field.

This indifference is all the more surprising in view of the fact that milling is such a widely used process in the rubber industry; in fact the great majority of rubber products undergo milling at some stage of their manufacture. Other manufacturing processes are essentially similar in character to the milling process. A decade or more ago, when extremely rapid acceleration had not become so extensively used as it is today, problems of milling did not confront the industry to such a serious extent as they do today. With respect to the moulding of rubber products, modern practice has featured three developments:

- (1) The maximum utilization of relatively costly moulds by the adoption of very short times of cure.
- (2) The use of highly accelerated mixtures to make possible these very short cures.
- (3) The use of high temperatures of vulcanization for the same purpose.

Recent developments in the continuous vulcanization of rubber-covered wire at high temperatures, *i.e.*, up to 200° C, have shown that it is possible to reduce the time of vulcanization to fractions of a minute.

In view of these trends, it seems timely to investigate some possible means of measuring the capacity of rubber mixtures to be moulded. The appearance on the market of numerous accelerators with retarded or delayed action is good evidence of the interest in the subject. It is with a view to helping to place the whole subject on a systematic basis that the method and apparatus described in the present paper were developed.

NATURE OF THE CAPACITY OF RUBBER MIXTURES TO BE MOULDED

From a practical standpoint any problem in moulding involves the choice of mould, the form of which may be complicated, the maximum allowable pressure for the particular moulding operation, taking into account the strength of the mould and the properties of the material to be moulded, and the final choice of a rubber mixture which not only has the properties desired in the finished article for its particular service, but at the same time makes possible the most economical manufacture, *i.e.*, in general the shortest practicable time of curing.

The problem is solved only when, under the allowable pressure and at the temperature chosen, the rubber mixture flows rapidly, fills the mould com-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 3, pages 85-90, March 1942. This paper was presented at the International Rubber Congress, Paris, May 1940.

pletely, and then vulcanizes in a short time. If the acceleration is too rapid, the mixture sets up prematurely, with resultant incomplete flow. If, on the other hand, the acceleration is moderate, but the mixture is not sufficiently plastic, the mould will not be filled completely before vulcanization commences.

It is evident, then, that the chief factors involved in the capacity of a rubber mixture to be successfully moulded are the plasticity of the mixture and the rate of vulcanization in its initial stages.

Numerous investigations have been devoted to one or the other of these factors. It is possible to measure plasticity separately at a temperature at which vulcanization does not take place to a sufficient extent to cause serious errors in measurement. It is likewise possible to follow the progress of vulcanization in its initial stages, especially at low temperatures, thanks to the changes in plasticity, elastic recovery, mechanical properties, etc., which take place with increasing time of vulcanization at a constant temperature. But these detached data are informative only in showing the way in which these properties change; they do not show the true capacity of a rubber mixture to be moulded successfully. In particular, only mixtures which are closely related in character can be compared in this way. It is not possible, for example, to predict from Williams plasticity measurements and from the rate of vulcanization at 100° C the relative moulding properties of two mixtures, one of which is a pure-gum type, the other of which contains a high proportion of carbon black.

Finally, the capacity of a rubber mixture to be moulded, although usually judged by plasticity and rate of vulcanization, depends on numerous other factors which are not readily measured and which it is practically impossible to correlate. Among these factors are thixotropy, thermoplasticity, temperature coefficient of vulcanization, thermal conductivity, and friction on metal surfaces.

A priori then, a study of the behavior of rubber mixtures during moulding would seem to be very complex. This is as a matter of fact quite true if the subject is approached analytically by unrelated studies of the influence of each of these factors. Up to the present time the available data on this subject are for the most part concerned with one or another of the determinant factors in the behavior of rubber mixtures during their initial stages of vulcanization. Mention might, for example, be made of the work of Eliel¹ on the temperature coefficient of vulcanization and delayed-action accelerators, and the work of Buchan² on changes in plasticity during the initial stages of vulcanization. As a result of these investigations and of other similar ones, it is possible to draw certain general conclusions, which, however, are of little or no aid in the solution of industrial problems.

It seemed, therefore, to the present author that it would be of interest to develop a method for measuring directly the behavior of a rubber mixture during a moulding operation. For any such direct method of measurement to be of practical utility, it should be possible to obtain a single value which would characterize moulding behavior, yet which would actually be the resultant of the effects of different contributing factors. To our knowledge, only P.H. Mensier³, in still unpublished work, has so far attempted measurements of this kind. But the procedure which he used, although giving results of great interest, has the inconvenience of requiring, in the preparatory work and in the actual testing, precautions which make it difficult to standardize the procedure. In addition, Mensier's procedure is too slow for practical control work.

In the following pages, a relatively simple method is described which has the advantage of making it practicable to operate with very small test-specimens, and with rapidity and excellent reproducibility of results.

PRINCIPLE OF THE METHOD OF MEASUREMENT

As has already been mentioned above, various methods are used by the industry for milling synthetic resins with a view to judging the capacity of these materials to be milled satisfactorily. However, in practice, none of the apparatus which has been used is applicable in a simple way to rubber mixtures. It was necessary, therefore, to find an apparatus which would be suitable to these particular mixtures.

One of the possibilities which most naturally comes to mind is to measure the plasticity of the mixture with an ordinary plastometer, but at a temperature in the same range as that of vulcanization. In a compression plastometer, such as that of Williams, the following successive phenomena take place.

(1) The sample softens, becomes very plastic, and commences to compress very rapidly.

(2) At the end of a certain time, which is brief if the acceleration is rapid and the temperature is high, vulcanization starts to be appreciable, and the rate of compression slows up rapidly.

(3) Vulcanization progresses, there is no further compression, and the thickness of the test-specimen becomes constant.

If, instead of operating at the temperature of vulcanization, the test is carried out at a relatively low temperature, continued compression is ordinarily observed, at least for a very long time. Representative curves of compression as a function of time at two different temperatures are shown in Figure 1.

Two interesting characteristics in the compression curve for the higher temperature are evident, the limiting height of compression and the time necessary for the test-specimen to compress to this thickness. The easier and at the same time the more interesting property to measure is the limiting thickness. This depends on the same two factors that the behavior on moulding does, *viz.*, the plasticity and initial stages of vulcanization. The limiting thickness can, then, serve as a criterion of the behavior during moulding. However, the limiting thickness varies inversely with the ease of moulding, and therefore it is preferable to measure the changes in the moulding properties by the changes in the surface area of the test-specimen after compression. Since the volume of the test-specimen and its thickness after compression are known, this surface area can be calculated readily.

DESCRIPTION OF THE APPARATUS

It might seem that this measurement could be made simply with an ordinary parallel-plate plastometer. However, this type of instrument has serious faults. It is customary, for instance, to place the plastometer in an oven at constant temperature, and then to place the samples underneath the plastometer by opening the oven door. Although this may be satisfactory for temperatures of 70° or 80° C, it is certainly not so for temperatures around 140° C or for those which must be used for estimating the behavior of a rubber mixture during moulding. At these high temperatures it is difficult to maintain the system at a uniform temperature without recourse to various artifices, such as forced circu-

lation of air, very accurate thermostatic control, etc. In addition, each time the oven is opened, there is considerable cooling, and consequently much uncertainty as to the temperature when a reading is made.

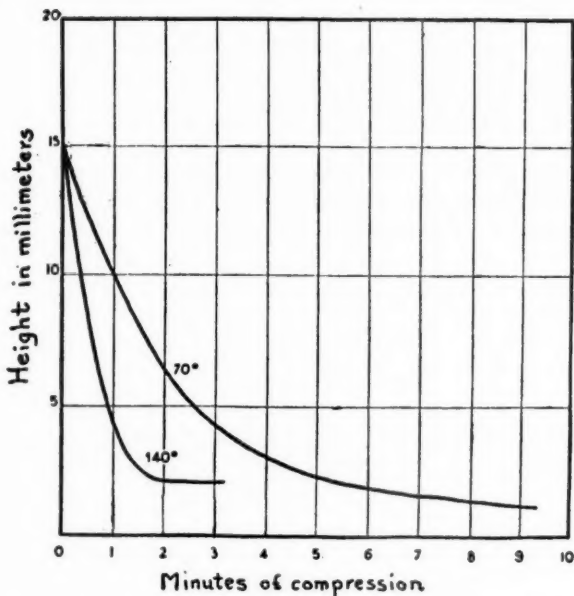


FIG. 1.—Compression of an accelerated mixture in a plastometer at 70° C and at 140° C.

In view of this, it was decided to construct an apparatus which would be better adapted to work at relatively high temperatures, and would embody the following features:

(1) The platens of the plastometer provided with individual resistances, so that it is possible to maintain a uniform temperature, adjustable at will between 50° and 220° C, over the entire surface of the platens.

(2) A very large surface area of the platens in relation to the size of the sample, so that uniform and reproducible conditions of heating are assured.

(3) A weight on the upper platen considerably greater than that of the Williams plastometer, *viz.*, 13.2 kilograms instead of 5 kilograms.

(4) Substitution of the strictly parallel displacement of the platens, which is difficult to control with heavy weights, by an angular displacement, whereby the upper platen is at rest in complete contact with the lower platen, and is raised from a horizontal axis located in the plane of the lower platen (see Figure 2).

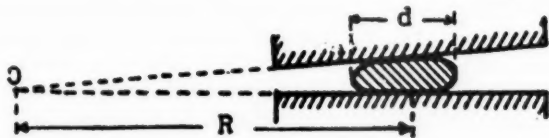


FIG. 2.—Angular displacement of the platens.

Under these conditions, the test-specimen is flattened in the form of a wedge and not strictly as a disc. However, the relative size of the test-specimen is very small compared to the radius of rotation, and the relative difference in thickness between the two extremities of the wedge is d/R , where d is 20 mm. and R is 500 mm., or only about 4 per cent. The overall shape of the test-specimen consequently differs only slightly from that of a true disc. This system, which is decidedly easier to operate than even a frictionless sliding system, gives almost the same results.

Figure 3 shows this apparatus schematically as constructed for practical use. The platens, B_1 and B_2 , are two identical units, made up of a cast-iron frame of parallelepiped shape, in which are inserted cast-iron heating platens, P_1 and P_2 . Heating resistances, R_1 and R_2 , of 600 watts and 220 volts, inserted in contact with these platens, make it possible to bring the platens to

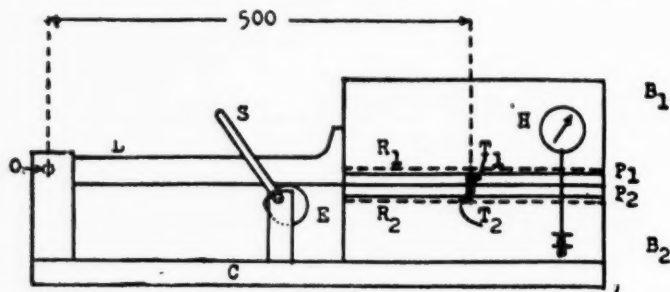


FIG. 3.—General assembly of the apparatus.

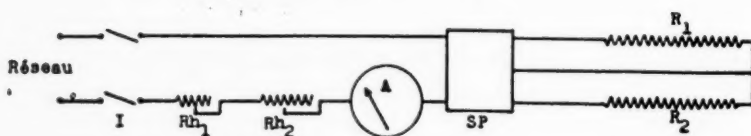


FIG. 4.—Scheme of the electric connections.

the desired temperature. In platens P_1 and P_2 are two drilled holes, T_1 and T_2 , 2 mm. in diameter, which terminate at the centers of the platens. Thermo-electric leads are inserted in these holes to measure the temperature.

The upper platen, P_1 , is united as one piece to a lever L , which is itself jointed at point O to the frame with its axis on ball bearings. The platen P_2 is united to a sectional iron frame. The upper platen P_1 can be raised easily by means of the eccentric operated by the lever S . The distance from axis O to the center of the upper block, P , is 50 cm.

Electrically, the assembly is equipped with a supply circuit for the heating resistance, comprising an ammeter, two control rheostats (one for rough control, the other for the final accurate adjustment), and a commutator in parallel series.

The temperature of the blocks is measured by copper-constantin thermo-electric couples, connected by a commutator to a millivoltmeter graduated directly in temperature and provided with a cold-joint temperature compensating device. A reading can be made within 0.5° .

Before the apparatus is used for any measurement, it should be checked to make certain that the two platens remain steadily at the same temperature. If this is not so, adjustment is made by inserting auxiliary resistance.

A micrometer with dial *H*, attached to the upper platen *P*₁, the pointer of which rests on a support with screw adjustment, makes it possible to record changes in thickness. This micrometer is adjusted to its zero reading when the platens are in contact, so that it will indicate at any moment the thickness of the test-specimen.

A measurement is carried out in the following manner. If the apparatus is cold, the platens are heated rapidly to the desired temperature by connecting them in parallel. In this way it is possible to reach a temperature of 140° C in five minutes. When the desired temperature is reached, the resistances are connected in series, and the current strength is adjusted to the point at which the temperature remains constant throughout the measurement. To this end a table of current strengths as a function of the temperature should be prepared for convenience of operation. Control of the temperature is facilitated by operating two rheostats. Experience has shown that thermostatic control is not indispensable, since deviations in the temperature during the time required for a measurement do not exceed 1° C.

The next operation is to raise the upper block by means of the hand lever *S*. The test-specimen is then placed in the center of the lower platen by means of pincers. This center point is located more easily if a circle is marked on the lower platen. The upper block is then lowered gently, and simultaneously a chronometer is started.

When the thickness reaches a fixed point, the upper block is raised by means of the eccentric, and the test-specimen is removed by pincers. It is sometimes necessary to leave the test-specimen on the platen for several minutes to prevent its sticking to the platen.

INFLUENCE OF THE OPERATING CONDITIONS AND THE CHOICE OF A TESTING TECHNIQUE

It was decided to examine briefly the influence of the operating conditions on the measurements, and to develop a technique which would be satisfactory for the purpose.

First of all, the following mixture was chosen:

Smoked sheet rubber	100
Sulfur	2.5
Zinc ethylphenyldithiocarbamate	1
Stearic acid	2
Zinc oxide	5

A comparatively rapid accelerator was chosen with a view to making the initial stage of vulcanization particularly well defined.

INFLUENCE OF THE SHAPE OF THE SPECIMEN

In measuring plasticity by the Williams plastometer, the most common practice is to use test-specimens roughly cylindrical in form, and cut from a thick sheet by means of a special machine which cuts a constant volume of 2 cc. In doing this, it is assumed that considerable variations in dimensions and shape have only a relatively small influence on the final result.

To ascertain whether this is true of rubber mixtures when moulded, test-specimens of various shapes and sizes were tested, including cylindrical test-

pieces 2 cc. in volume and of heights ranging from 0.5 to 2 cm., cubical test-pieces, paralleloiped test-pieces, pyramidal test-pieces, etc. All the specimens were tested at 140° C, their minimum thicknesses determined, and the corresponding surface areas were calculated. Three test-specimens of each size and shape were tested, and the mean of each set of three measurements was taken as the characteristic value.

The following tabulation gives the results obtained with cylindrical test-specimens.

Thickness of specimen (in cm.)	0.5	0.75	1	1.25	1.5	1.75	2
Limiting surface area	11.9	12.1	12.3	12.5	12.7	12.8	13

It is evident from these values that considerable differences in dimensions result in relatively small differences in surface area. In practice the use of a cylindrical test-specimen 1 to 1.5 cm. thick and 2 cc. in volume makes the influence of shape negligible. This test-specimen can be cut out either by a punch-die from a sheet of the proper thickness or by an automatic machine designed for cutting out test-specimens for the Williams plastometer. If the specimens are cut out with a punch die, it is necessary to tare them to the exact weight corresponding to a volume of 2 cc. This taring operation can be carried out very conveniently by means of an automatic precision balance, which gives a direct reading to 1 cg. for masses of 0 to 5 grams.

It seems unnecessary to describe in detail all the tests which were made with test-specimens of various forms other than cylindrical. Suffice it to say that the part played by the original shape of the test-specimen is negligible provided that certain conditions are fulfilled. First of all, the general form should be that of a paralleloiped, and pyrimidal shapes should be avoided. Secondly, the cross-section of this paralleloiped should be of symmetrical form, *i.e.*, a square, circle, or regular polygon, rather than a form which emphasizes any particular dimension, *e.g.*, rectangle or parallelogram. Finally, the thickness of the test-specimen should lie within the range of 1 to 1.5 cm.

ACCURACY OF THE MEASUREMENTS

To determine the accuracy of this method of measurement, twenty successive tests were carried out with cylindrical test-specimens 10 mm. high and 2 cc. in volume, cut from a single sheet of the mixture given above (Mixture No.1). The results of the tests are tabulated below.

No. of test-specimen	1	2	3	4	5	6	7	8
Limiting surface area	12	12	12.1	12.2	12.2	12.3	12.3	12.3
No. of test-specimen	9	10	11	12	13	14	15	16
Limiting surface area	12.3	12.4	12.4	12.4	12.4	12.4	12.5	12.5
No. of test-specimen	17	18	19	20				
Limiting surface area	12.5	12.6	12.6	12.6				

The accuracy of the method is obviously excellent, the maximum deviation being 4.9 per cent of the mean value, and the absolute mean deviation being only 2.9 per cent.

INFLUENCE OF THE VOLUME

It was of interest next to ascertain according to what law the limiting surface varied as a function of the volume. To this end a series of test-specimens was prepared, the volumes of which ranged from 0.5 to 5 cc., and which were cut

from the same sheet (Mixture No. 1), and which were, therefore, of the same height (15 mm.). The following results were obtained:

Volume (cc.)	0.5	1	1.5	2	3	4	5
Limiting surface (sq. cm.)	6.6	9.1	10.7	12.5	15	17.2	20.9

The general trend of the change in surface with increase in volume, which can be seen in Figure 5, is that of a parabolic function. The relative change in the limiting surface with change in volume is particularly great for small volumes. Since it is important to reduce the magnitude of the deviations in surface area and thus to reduce the causes of errors from accidental differences in volume, a volume of 2 cc., which falls within the region of relatively small change in surface area with increase in volume, has been chosen for practical purposes.

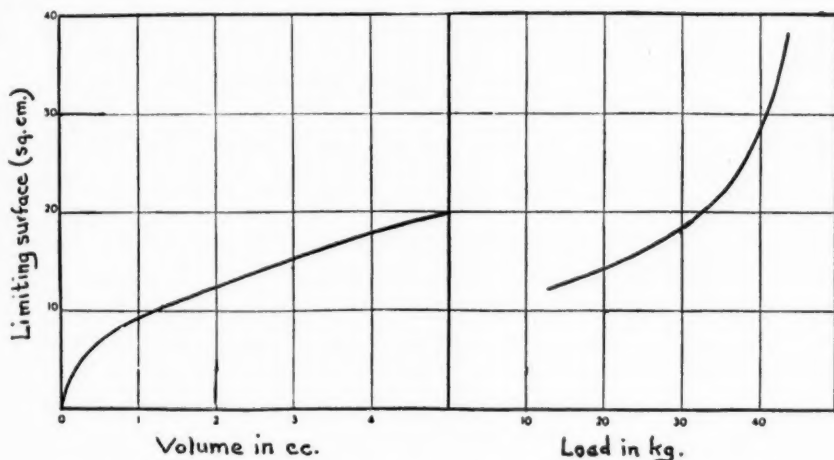


Fig. 5.—Limiting surface as a function of the volume of the test-specimen.

Fig. 6.—Limiting surface as a function of the loading.

INFLUENCE OF THE COMPRESSIVE LOAD

The influence of the weight of the upper platen was studied by changing this weight of 45 kilograms. In this case cylindrical test-specimens, 2 cc. in volume, 10 mm. high, and cut from a sheet of the same mixture as before (No. 1) were used. The following results were obtained.

Total load (kg.)	13.2	18.2	23.2	28.2	33.2	38.2	43.2
Limiting surface area (sq. cm.)	12.5	14	16	18.2	19.0	26.8	36.5

The limiting surface area is seen to increase more rapidly than does the total load (see Figure 6). Hence it should be possible to increase the sensitivity by taking advantage of this effect of heavy weights.

INFLUENCE OF TEMPERATURE

The influence of the temperature from 70° C to 200° C was studied, again with the same rubber mixture (No. 1) and with the same kind of test-specimens used for studying the influence of the load (see Figure 7). The following results

were obtained:

Temperature (°C)	70	80	90	100	110	120	130	140	150
Limiting surface area	40	36	33	31	22.2	16	14.3	12.3	12
Temperature (°C)	160	170	180	190	200	220			
Limiting surface area	11.5	11	10.5	10.5	10.5	10.5			

It should be pointed out that the time required to reach the limiting thickness depends greatly on the temperature. It is only a few seconds at 200° C, whereas it is several hours at 170° C. Attention should be called to a very curious phenomenon which is evident at temperatures above 170° C. In the range above 170° C, the limiting thickness is reached very rapidly, whereupon the test-specimen remains unchanged for a certain length of time which de-

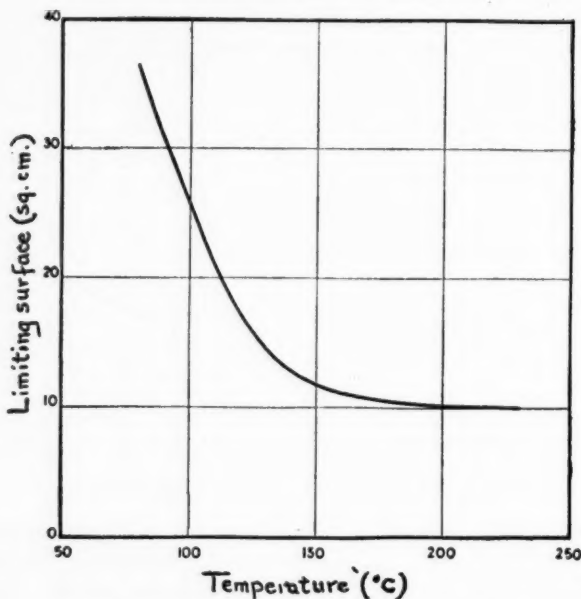


Fig. 7.—Limiting surface as a function of the temperature.

depends on the temperature. But following this, it increases in thickness, and at least in the case of the particular rubber mixture which was studied (No. 1), appreciable reversion becomes evident, with increasing stickiness and ultimate total decomposition. It is probable that the increase in thickness is caused by the liberation of gases formed by pyrolytic decomposition. In cases like this, there is a point of minimum thickness of the test-specimen.

CHOICE OF OPERATING TECHNIQUE

From what has been described in the preceding paragraphs, it is possible to work out a satisfactory testing procedure.

1. *Type of test-specimen.*—Volume 2 cc. Height 10–15 mm. Cylindrical form.
2. *Temperature.*—140° C. At this temperature the influence of vulcanization is very evident in its effect on the plasticity; the test is rapid; the time to

reach the limiting thickness varies (according to the acceleration) from one-half minute to 2 minutes, and the total time necessary to assure easy removal of the specimen from the platen varies from 2 to 5 minutes. Furthermore, at this temperature and with the majority of ordinary rubber mixtures, reversion appears only after considerably longer times.

3. *Compression load.*—A weight of 13.2 kilograms is sufficient for satisfactory sensitivity. In special cases recourse can be had to heavier loads.

By following this testing procedure, tests can be carried out in a very short time. It is sufficient to test three specimens for each rubber mixture. Since each individual test requires 2 to 5 minutes, it is possible to prepare between times samples for the subsequent tests. In the case of mixtures which are to be moulded but which vulcanize rapidly, it is possible for an experienced operator to test six or seven different rubber mixtures per hour. This is a very satisfactory mode of operation.

REPRESENTATIVE APPLICATIONS

Within the limits of this brief presentation of the subject, it is not the intention to describe all the possible applications of this new testing procedure, but a few representative cases may be pointed out.

COMPARISON OF ACCELERATORS

The following mixtures were prepared:

	(2)	(3)	(4)	(5)	(6)
Smoked sheet rubber	100	100	100	100	100
Stearic acid	2	2	2	2	2
Sulfur	2.5	2.5	2.5	3	8
Zinc oxide	5	5	5	5	5
Accelerator R	0.5	—	—	—	—
Accelerator TM	—	0.2	—	—	—
Accelerator GS	—	—	0.8	—	—
Accelerator DPG	—	—	—	1	—

These mixtures were masticated so as to obtain a uniform plasticity in each case, as judged by separate tests with a Williams plastometer. They were then tested for their behavior on being moulded, in accordance with the testing procedure described above. The results of the tests were as follows:

	(2)	(3)	(4)	(5)	(6)
Plasticity (Williams)	380	290	285	280	285
Limiting surface area	13.8	14.3	28.5	15.4	32
Time to reach limiting thickness (min.)	0.5	0.5	2	1	6

These results show the different results which can be obtained with different accelerators; *e.g.*, accelerator *GS* gave excellent results, both compared to the more rapid accelerators *R* and *TM* and compared to *DPG*. It is somewhat surprising at first thought that *DPG* should give poorer results than *GS*, when the optimum of cure of the mixture accelerated by *DPG* was longer than that of the mixture accelerated by *GS*. However, this confirms practical observations. Accelerator *GS* may be regarded as a delayed-action accelerator; *DPG* as an accelerator which is at the same time slow and prematurely active. So far as behavior on moulding is concerned, the difference between the mixture accelerated by *GS* and the less actively accelerated mixture is small. This means that a proper choice of accelerators makes it possible to solve all problems of moulding which can be solved by the use of weakly accelerated mixtures.

COMPARISONS OF FILLERS

Several currently used fillers were compared. In this case the rubber mixtures were all of the same hardness (measured with a Shore instrument) after vulcanization. Before vulcanization the mixtures were plasticized, both by mastication and by the addition of vaseline oil, until they had the same approximate Williams plasticity values.

Smoked sheet rubber	100	100	100	100
Sulfur	2.5	2.5	2.5	2.5
Accelerator GS	1	1	1	1
Stearic acid	2	2	2	2
Vaseline oil	—	2	—	5
Zinc oxide	200	—	—	—
P-33 Black	—	80	—	—
Whiting	—	—	100	—
Colloidal clay	—	—	—	90
Plasticity (Williams mm.)	3.2	3.2	3.2	3.2
Hardness (Shore; vulcanized)	65	65	65	65
Limiting surface area (sq. cm.)	20.1	12.3	16.5	18.5

It is evident that when the plasticities were practically the same, different fillers gave different ease of moulding. These different effects are probably related in some way to their different activities during vulcanization, *e.g.*, it is known that P-33 Black is an active accelerator.

VULCANIZATION AT HIGH TEMPERATURES

The results of a series of tests with Mixture No. 1 at widely different temperatures have already been described, and it has been shown that the ease of moulding, as measured by the limiting surface, does not continue to decrease indefinitely with increase in temperature. It should be possible, therefore, by the use of high pressures, to obtain good moulding even at very high temperatures. This possibility becomes still greater in view of the way in which they limiting surface area varies with the pressure, *viz.*, the surface area increases to a disproportionately great degree with increase in pressure (see Figure 6). The problem of moulding at high pressures can, therefore, from the standpoint of complete filling of the moulds, be solved by the proper choice of accelerators and conditions of moulding. The greatest difficulty is to cool the moulded products rapidly enough to avoid the reversion which is likely to set in so rapidly at very high temperatures. In this respect there are doubtless many suggestions to be obtained from the equipment and operations used in moulding plastics.

POSSIBLE IMPROVEMENTS

The apparatus and method which have been described are certainly open to various improvements. One of the most interesting would without doubt be the addition of a recording device with which an autographic record of the curve of thickness as a function of time could be obtained. The present author is now attempting to develop some such device. A device which would make it possible to vary the load through a much greater range would likewise be of the greatest interest. It should be possible to explore a range of pressures from 2 or 3 kg. per sq. cm. to moulding pressures as high as 1000 kg. per sq. cm. or even higher.

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PRACTICAL APPLICATIONS

Even in its present form, the new apparatus can be of service in numerous ways. As a control method in manufacturing operations, it will give more enlightening information than simple measurements with a plastometer, and much more quickly than do measurements with a Williams plastometer.

In investigations concerned with various rubber mixtures and the proper choice of compounding ingredients, particularly accelerators, the apparatus makes it possible to avoid trial-and-error experiments and to reduce to a minimum manufacturing trials.

In the selection of a rubber mixture which will be suitable for a particular moulding operation, the procedure would be to test a series of rubber mixtures of various physical properties and with decreasing ease of moulding. The limiting surface area of that mixture which is the last in the series to mould satisfactorily is measured. The final mixture can then be developed to fulfill satisfactorily all the required moulding conditions, both from the point of view of the properties, the finished article and from that of moulding.

CONCLUSION

The simplicity of the method, its adaptability to the most varied needs, and the ease of construction of the apparatus, are good reasons why it is certain to lead to interesting developments. By utilizing it properly, it is possible to simplify greatly the various problems involved in the development of new rubber mixtures and to avoid the necessity of factory experiments, which are always burdensome.

REFERENCES

¹ Eliel, *Trans. Inst. Rubber Ind.* 12, 161 (1936-37).

² Buchan, *Trans. Inst. Rubber Ind.* 12, 309 (1936-37).

³ Mensier, P. H., Unpublished experiments on the capacity of rubber mixtures to be moulded.

MEASUREMENT OF THE PLASTICITY OF BUNA-S WITH THE WILLIAMS APPARATUS *

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In processing raw materials such as reclaimed rubber, polyvinyl chloride and Buna-S on an industrial scale, it is necessary to use auxiliary materials known as plasticizers. This general designation comprises a wide variety of materials, and these plasticizers do not have the same effects in the different raw materials to which they may be added. To process Buna-S successfully it is necessary first to plasticize it, *e.g.*, by degrading it thermally and adding products such as anthracene oils. The object of such treatment is to diminish the nerve of the elastomer and to render subsequent mixing easier. On the contrary, to impart elastic properties similar to those of rubber to polyvinyl chloride, products such as tricresyl phosphate and butyl phthalate are added, yet these likewise are generally designated by the name of plasticizers.

Thus in the one case, a plasticizer is used to diminish elasticity; in the other case it is used to increase elasticity. It is not surprising, therefore, that technologists are sometimes confused in evaluating the merits of so-called plasticizers.

In France, plasticity is generally determined with a Williams apparatus. The principle of the method is to compress a test-specimen of known volume under a definite weight at a constant temperature for a predetermined time, and then to measure the compression of the specimen. Following this, the load is removed, and the height to which the specimen recovers, *i.e.*, the elastic recovery, is measured.

The operating conditions have not been standardized. Although a sample of 2 cc. volume is almost always used, there are no generally accepted conditions of temperature and time of compression. Furthermore, practical difficulties which have been encountered in efforts to measure the plasticity of samples of synthetic elastomers have led to the conviction that the Williams apparatus is not suited to the measurement of the plasticity of this class of materials.

These difficulties can be avoided if account is taken of the fact that the Williams apparatus was devised to measure the plasticity of rubber and of rubber mixtures, and the compressive force and range of temperature were chosen for these materials. Consequently if any other material is to be tested successfully in the Williams apparatus, its plasticity must first of all be brought to the same order of magnitude as that of rubber. This similarity in plasticity is, moreover, necessary because these different raw materials are ultimately processed in more or less the same way in the same machines. If, for example, it is desired to measure the effect of a plasticizer on a sample of Buna-S which has not been degraded, it is almost impossible to interpret the results obtained if the Williams apparatus is used. In reality Buna-S has much more nerve than crude rubber if it has not been degraded thermally, and the Williams apparatus

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 19, No. 5, pages 165-166, June 1942.

is unsuitable for measuring the plasticity of this sort of material. On the contrary, the plasticity of degraded Buna-S can be determined quite reliably by this same method.

MEASUREMENT OF THE WILLIAMS PLASTICITY OF BUNA-S

In the experiments to be described, the procedure for measuring plasticity was as follows. By way of example, the plasticizing power of diphenylamine was studied. The Buna-S was thermally degraded by heating at 130° C in the presence of oxygen¹. The degraded Buna-S was milled on a cold laboratory mill for 20 minutes, 15 per cent of plasticizer was added, the mixture was milled for 20 minutes more, and the resulting mixture was moulded cold overnight into a sheet 8 mm. thick. From this sheet cylindrical test-specimens of a diameter of 18 mm. were died out. These test-specimens had a volume close to 2 cc. This volume was checked on a hydrostatic balance and adjusted with a razor if necessary.

To each of the mixtures, prepared in the way described above, was added 100 per cent of barium sulfate, based on the weight of Buna-S. These mixtures were milled for 20 minutes, and then on a cold mill for 10 minutes to assure complete dispersion. The products were finally moulded and test-specimens died out.

EXPERIMENTAL RESULTS

In using the Williams apparatus in the experiments to be described, the test-specimen was compressed under a weight of 5 kilograms at a temperature of 70° C. The elastic recovery was measured under a weight of 300 grams at the same temperature. The thickness of the test-specimen was measured each minute for 5 minutes of compression and again each minute for 5 minutes of elastic recovery. Before each series of measurements, the test-specimen was allowed to rest in the oven at 70° C for at least one hour.

TABLE 1

UNLOADED MIXTURE

Thickness of Test-Specimen After Increasing Times of Compression and Recovery

Minutes	Without plasticizer	With diphenylamine
1	5.03	3.88
2	4.71	3.63
3	4.54	3.48
4	4.45	3.38
5	4.34	3.30
6	4.82	3.44
7	4.99	3.49
8	5.09	3.51
9	5.18	3.53
10	5.24	3.54
Elastic recovery	0.90	0.24

The elastic recovery is designated as the difference between the thickness after compression and the thickness five minutes after release of the weight of 5 kilograms. Tables 1 and 2 give the results obtained with the mixtures con-

taining no plasticizer and with the mixtures containing diphenylamine. Each value is the mean of three measurements.

TABLE 2
LOADED MIXTURE
Thickness of Test-Specimen After Increasing Times of Compression and Recovery

Minutes	Without plasticizer	With diphenylamine
1	5.09	4.34
2	4.69	4.03
3	4.49	3.91
4	4.36	3.79
5	4.26	3.70
6	4.52	3.85
7	4.60	3.90
8	4.66	3.92
9	4.70	3.94
10	4.73	3.95
Elastic recovery	0.47	0.25

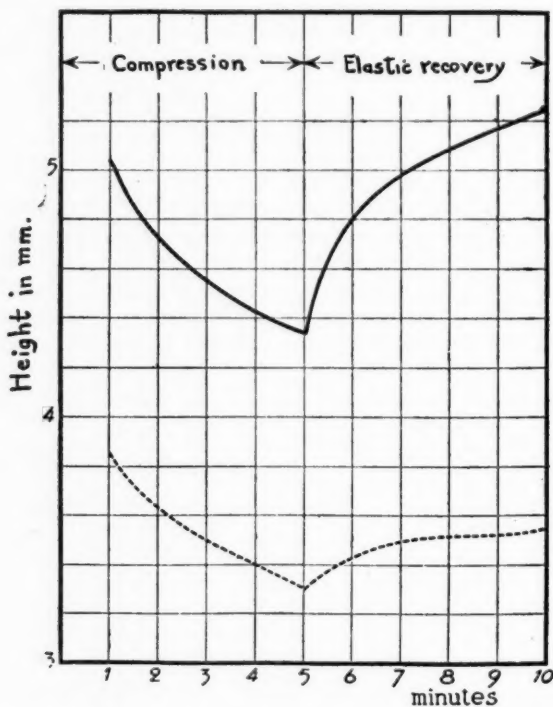


FIG. 1.—Mixture containing no filler. The curve with solid line represents the mixture without plasticizing agent; the curve with a broken line represents the mixture with plasticizing agent RVD.

From the data in Tables 1 and 2 curves can be constructed to show the behavior of the two mixtures more plainly. It is evident that the plasticizer diphenylamine increases considerably the compression and reduces the elastic recovery.

This example shows that it is easy to follow changes in the plasticity of Buna-S by means of the Williams apparatus within the range to be expected in processing this material with equipment in general use in the rubber industry.

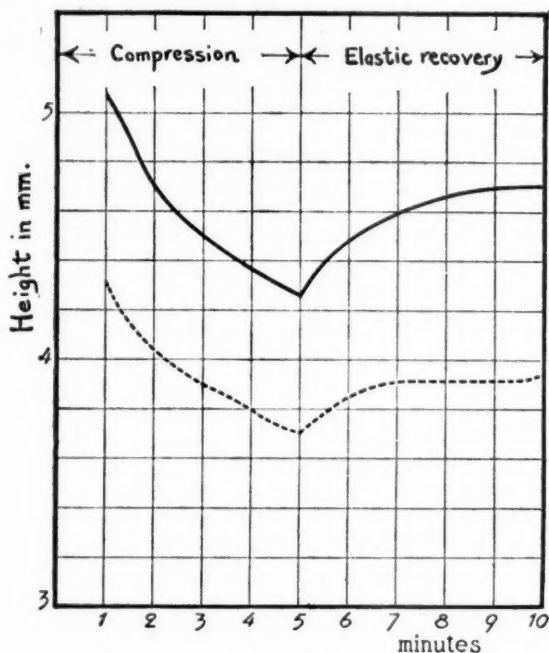


FIG. 2.—Loaded Mixture. The curve with solid line represents the mixture without plasticizing agent; the curve with a broken line represents the mixture with plasticizing agent RVD.

REFERENCE

- ¹ Springer, *Kunststoffe* 30, 285 (1940); *Kautschuk* 16, 72 (1940).

NEW METHOD FOR DETERMINING THE FILLER CONTENT OF VULCANIZED RUBBER *

R. A. HUBLIN

One of the analytical problems most frequently encountered in the rubber industry is the determination of the inorganic and organic filler contents of a rubber product. There are various solutions to this problem, which differ both in their general utility and in their accuracy. These various methods can be divided into two general groups:

- (1) methods which involve calcining the sample.
- (2) methods which involve solution of the sample.

The methods of the first group have inconveniences which are so well recognized that it is unnecessary to discuss them at length at this time. Their most serious disadvantage lies in the errors which are likely to occur when the rubber sample contains carbon black or ingredients, such as carbonates, sulfides, hydroxides, etc., which decompose or oxidize at the temperature of calcination. Of course when the calcination method is used merely as a control test for a product of known composition, the method is rapid and very useful.

However, because of the impossibility of overcoming satisfactorily, without added irremediable complications, the inconveniences mentioned, most analysts have made efforts to replace these calcination methods by solution methods. With a solvent which dissolves vulcanized rubber at a sufficiently low temperature, it is possible to separate the fillers without danger of decomposing them. Several methods of this kind are in practical use today, *e.g.*, the method specified by the American Society for Testing Materials¹, which involves solution in mineral oil, and similar procedures used by the O.C.E.M., and in the specifications of the French railways². Of the same general character is the method of Pontio³, which involves extraction with cumene. The first two of these methods are extremely useful, and their precision is quite satisfactory; yet they too have certain practical inconveniences.

Mineral oil is, in effect, a solvent for vulcanized rubber only at relatively high temperatures, and to obtain reasonably rapid solution in practice, it is necessary to work at temperatures at least as high as 150° C. Under these conditions, and particularly when the products to be analyzed are heavily loaded or contain reclaimed rubber, solution is very low. In such cases an effort is usually made to hasten the process of solution by raising the temperature. But when this is done, a new source of serious errors is introduced. The sample to be analyzed and the solvent itself carbonize to a certain extent, and thereby add appreciable amounts of insoluble residues to the remaining liquid, and this leads to incorrect weights of filler. This source of error is familiar to all chemists who have used the method described in the specification² of the French Railways. Even when this procedure is followed scrupulously, the analytical results show filler contents which are very frequently too high, as judged by analyses of mixtures of known compositions.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 17, No. 2, pages 49-50, February-March 1940.

One must then be reconciled either to an analytical procedure which is slow and tedious, or to obtaining results which are in error to a certain extent. In addition it frequently happens that separation of the fillers from the solvent is very difficult. With carbon black especially, colloidal suspensions are formed, the stability of which is favored by the viscosity of the oil. Even after dilution, the filtration process is long and at times uncertain.

With a view to overcoming these drawbacks, the present author has made an effort to find a solvent with which solution can be effected in a reasonably short time, and at a sufficiently low temperature to avoid all carbonization and at the same time to avoid the difficulties of sedimentation and filtration.

A first and useful clue to the solution of the problem was found in a passage in the now old work of C. O. Weber⁴, in which this author describes a method of analysis which utilizes as the solvent either α -nitronaphthalene or nitrobenzene, the latter being particularly effective for mixtures having low coefficients of vulcanization. These two solvents were studied thoroughly by the present author. The results obtained with α -nitronaphthalene in particular were excellent so far as the rapidity of solution was concerned. Even mixtures with high reclaimed rubber contents or with high percentages of carbon black, which can be dissolved in mineral oil only with difficulty, passed completely into solution in α -nitronaphthalene in one-half to one hour at 160–170° C. This in itself was an important step forward. However, certain inconveniences were encountered with this method too. At ordinary temperatures, α -nitronaphthalene is a solid and, after the solution is complete, it recrystallizes in the receptacle. It is necessary to redissolve it in a large excess of a solvent, and when the liquid is filtered the edges of the filter become covered with a crystalline efflorescence which entrains solid particles and makes thorough washing very difficult. Moreover, there is still carbonization to a considerable extent, in spite of the short time required for complete solution, because of the relatively high temperatures which must be used. It is easy to verify this by analyzing mixtures of known compositions.

Nevertheless the results described above represent at least one step forward, a considerable speeding up of the operations. The next step was to determine whether this was attributable to the presence of the nitro group in the α -nitronaphthalene. To this end the tests were repeated, using pure naphthalene as the solvent. It was found that, in this hydrocarbon, solution required a much longer time than in α -nitronaphthalene. This indicated that the nitro group has a very favorable effect.

Memmler has already reported⁵ that anisol can be used as a solvent for vulcanized rubber, with the advantage that temperatures as low as 100° to 120° C can be used. It is true that at this temperature anisol can be used, but the time required for complete solution is then about the same as that necessary with mineral oil at 150° C. However, at least the danger of carbonization and decomposition of some fillers, *e.g.*, antimony trisulfide, is practically eliminated. But anisol is rather expensive, so recourse was had to *o*-nitroanisole, with the hope that the presence of the nitro group, as in the case of α -nitronaphthalene, would have the effect of accelerating greatly the dissolution process. Experiments showed that this assumption was correct, for this new reagent dissolved in very short times, *e.g.*, 20 to 60 minutes, and at mild temperatures, *e.g.*, 100° to 120° C, samples which were extremely resistant to the action of mineral oil.

By the use of *o*-nitroanisole, then, it becomes possible not only to operate at relatively low temperatures but also to avoid at the same time all carbonization and all decomposition of the fillers, and in addition to carry out the procedure

rapidly. It was found also that *o*-nitroanisol has much less tendency to form colloidal suspensions of the fillers than do oils. Consequently sedimentation is in general rapid and complete. Various kinds of materials can be used as diluents, *e.g.*, benzene, toluene, petroleum ether, chlorinated solvents, etc. A mixture of equal parts of toluene and carbon tetrachloride is a very satisfactory diluent for practical use. The toluene should be carefully rectified and should be absolutely free of heavy residue. This diluent can be kept over dry sodium sulfate.

The precision of the method with *o*-nitroanisol was carefully confirmed with mixtures of known compositions, and containing a wide variety of fillers, including carbon black, other blacks, whiting, zinc oxide, barytes, silica, slate flour, magnesium carbonate, clay, etc. In all cases it was found that, with the correct technique, values within approximately 2 per cent of the correct values were obtained. This precision is decidedly better than that obtained with either the A.S.T.M. method¹ or French Railways method², neither of which ordinarily gives values closer than 5 per cent of the correct values, especially in the presence of carbon black. Contrary to its effect when the A.S.T.M. method or French Railways method is used, reclaimed rubber does not prolong beyond reasonable limits the time required for solution.

The procedure which was finally adopted is as follows.

Treatment of the sample before dissolution.—Preliminary treatment of the sample is carried out according to the specifications of the American Society for Testing Materials⁶ or those of the French Railways².

Dissolution of the sample in o-nitroanisol.—After preliminary treatment as specified above, weigh 1 gram of sample, finely divided by grinding on a tightly set experimental mill or by cutting into pieces not larger than 1 mm. on a side. Then place the sample with about 25 cc. of *o*-nitroanisol in an Erlenmeyer flask of 100-cc. capacity, equipped with a vertical air-cooled condenser and thermometer. The reservoir of the thermometer should be entirely immersed in the liquid. It should be made certain that the *o*-nitroanisol contains no inorganic impurities nor any trace of acidity. Heat the flask and its contents on an oil bath, controlling carefully the rise in temperature and then regulating the heating so as to maintain the temperature of the thermometer around 115° C. As soon as this temperature is reached, it is maintained thus for 30 minutes. In the great majority of cases, this period of time is sufficient for complete solution. If it is not, the digestion may be continued 30 minutes longer.

Sedimentation and filtration.—After cooling, dilute the contents of the Erlenmeyer flask with 150 cc. of toluene-carbon tetrachloride mixture, and allow to stand until sedimentation is complete. In the absence of carbon black, this sedimentation is very rapid, whereas it requires several hours if carbon black is present. Cover the flask with a small watch-glass. Completion of sedimentation is easily recognized. Prepare a tared filter (slow-filtering Ruby Red Durieux paper is suitable) which has been previously extracted with carbon tetrachloride. Special filter paper free of all extractable fats or oils is also acceptable. Filter the decanted liquid very carefully, with return to the filter for further filtration until the filtrate is no longer turbid. This filtrate is in most cases brownish, with the usual appearance of colloidal suspensions. A black coloration indicates bad filtration. When the filtration of the supernatant liquid is complete, filter the fillers with the aid of a wash bottle containing the diluent mixture. Wash thoroughly with this same hot liquid until all organic material is completely removed, dry the tared filter at 70° C, and weigh.

APPLICATIONS

Aside from the direct determination of the filler contents of rubber mixtures, the method which has been described is very useful for determining the weight of rubber with which a fabric is impregnated or coated. It is possible, for instance, to determine easily the coating of a waterproofed fabric or the weight of the rubber friction in a belt fabric. It should be mentioned that, thanks to the use of low temperatures and relatively short times of treatment, cotton fabrics are very little affected during removal of the rubber. It is, possible, therefore, after extraction of the rubber, to test them for their mechanical properties, so that the results obtained have some significance. Of course in this case standard test-specimens of the fabric are out of the question, but a good idea of the quality can be had by cutting out small strips 1 cm. \times 5 cm. from the important part of the product. These test-specimens are broken in a rubber dynamometer, with a tractive speed of 100 mm. per minute. To be able to interpret correctly the results of such tests, it is advisable to test in the same way a fabric of similar construction and of known characteristics, and one which has undergone similar treatment, such as frictioning, coating, vulcanization, and removal of the rubber by solution in *o*-nitroanisol. Instead of tensile tests, it is possible to make bursting tests of small samples, in the form of discs, by an apparatus similar to apparatus used in the paper industry.

CONCLUSIONS

The new reagent, *o*-nitroanisol makes it possible to shorten to a considerable extent the determination of the total filler content of vulcanized rubber, and to increase the precision of the determination. In addition, the procedure is carried out more easily than are the older classic procedures. It would seem desirable, therefore, to use this more convenient solution method of determining filler content in many cases in place of calcination methods, which, though rapid, are very inaccurate, and in place of the conventional solution methods, which are so inconvenient.

REFERENCES

- ¹ A.S.T.M. Standards on Rubber Products, standard methods of chemical analysis of rubber products, Specification D297-36, pp. 83-104.
- ² O.C.E.M. des Chemins de Fer français, Partie Analytique, Specification no. 47.
- ³ Pontio, "Analyse du Caoutchouc et de la Gutta-percha." Edited by Gauthier-Villars, Paris. Weber, "The Chemistry of India Rubber," Griffin, London, 1902.
- ⁴ Memmler, "Production et Traitements du Caoutchouc, Dunod, 1935, p. 407.
- ⁵ A.S.T.M. Standards on Rubber Products, standard methods of chemical analysis of rubber products, Specification D297-36, Part B, paragraph 45.

THE CONCENTRATION OF LATEX BY MEANS OF ELECTRIC CURRENTS OF HIGH FREQUENCY *

HENRI LEDUC AND RENÉ DUFOUR

The rubber industry has at its disposal various types of latex which may conveniently be divided into two general groups: (1) latices with a normal content of dry solids, including ordinary latex stabilized with ammonia; and (2) concentrated latices. The first group comprises latices which contain 38 to 40 per cent of dry solids; the second group comprises latices which frequently contain 60 to 70 per cent, and sometimes even more, of dry solids.

Concentrated latices can in turn be divided into three important categories, according to their method of preparation: (1) latex concentrated by centrifugation; (2) latex concentrated by creaming, and (3) latex concentrated by evaporation.

Revertex belongs to this last category. Concentration was first carried out in a bowl rotating around an inclined axis and heated externally by a current of hot water circulating in a double jacket. Subsequently the latex was concentrated by spraying it while hot into an evaporating chamber. In this operation, a certain amount of water is eliminated, and the more concentrated mass which collects at the bottom of the evaporating chamber is again heated and returned to the chamber. The cycle is continued until the desired concentration is reached. The preheater is constructed of a set of tubes immersed in a current of hot oil.

Fresh latex, which is less stable than older latex preserved with ammonia, soon deposits a layer of rubber on the walls of the tubes, which retards heat exchange, and makes it necessary to take the exchanger apart to be cleaned. This operation must be repeated several times each day, and this complicates the operations and increases the cost of production. There is the added loss of material through the actual rubber deposited on the walls of the apparatus.

This objectionable feature can be avoided by the replacement of the heat exchanger and its oil bath by a suitably arranged high-frequency current heating unit. In this way a high-frequency current makes it possible to develop heat within the liquid to be heated, and thus to utilize a set of tubes made of glass ceramic ware or other inert material. It is even possible to maintain the temperature of the walls of the heater below the temperature of the circulating liquid, thus minimizing the danger of coagulation.

In the discussion which follows, it will be pointed out why and how the same results can be obtained with high-frequency currents. The first subject to be considered is the behavior of an aqueous liquid, such as latex, when it is placed in an electric field of high frequency. Suppose, for example, that a prismatic trough made of a material which is essentially nonconducting, *e.g.*, glass, is placed between the electrodes of a condenser supplied with a high-frequency current, with the sides of the trough set parallel to the plane of the

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metal plates which form the condenser (see Figure 1). The charges which appear on the sides of the trough with each reversal of the current will then be dissipated as resistance, and this will increase the temperature by the Joule effect (not by electric losses, such as happens in a mass of rubber in the case of radiovulcanization). Figure 2 shows this assembly schematically.

But since this method involves the heating of a liquid conductor by an electric resistance, the question may well be asked why two electrodes connected to the terminals of an ordinary electric generator should not be immersed in the liquid. The answer is simple. If the current is continuous, one of the

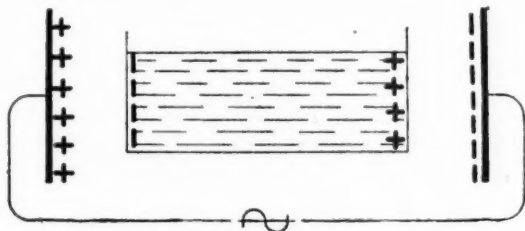


FIG. 1

electrodes becomes covered with a cataphoretic deposit of rubber, which is creamy at first, but then coagulates, and soon obstructs all further passage of the electric current. It might be remarked in passing that an assembly of this kind has been recommended for concentrating latex, and that the manufacture of rubber articles by cataphoretic deposition is well known.

When an alternating current is employed, one is still dealing with electrolysis, but although in this case it is much slower than it is with a continuous current, it is still far from negligible, and here too the electrodes become covered with a deposit of rubber. On the contrary, if resort is had to the high

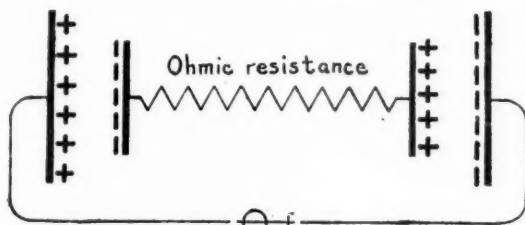


FIG. 2

frequency method, there is no longer any electrolysis to be considered. Better still, there is no need of electrodes, so all contact of the latex to be concentrated with metal is avoided, and consequently there is no danger of corrosion or contamination of the latex.

In practice it is advisable to use, in place of the prismatic trough, some sort of assembly which makes certain the systematic circulation of the latex in the electric field before it is conveyed to the evaporator, *e.g.*, a circular trough into which the latex is run through a central pipe and flows to the periphery of the circular trough (see Figure 3). It is, however, possible to employ a heating

unit composed of one or several insulating tubes through which the latex flows. Along these tubes are placed ring electrodes (see Figure 4) or plate electrodes parallel to the ends of the tubes and on the outside of them.

A method which has the advantage of simplicity is to concentrate the latex in a rectangular tank at constant level. The latex is kept agitated by an air current blown into the mass, and this air entrains water vapor evolved during the operation. When the desired concentration is reached, the apparatus is emptied, and filled with a new charge of latex.

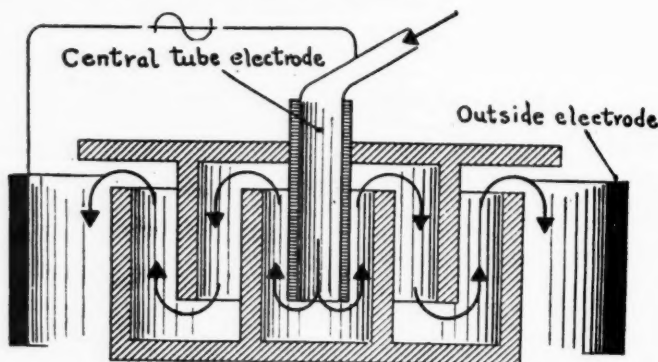


FIG. 3

Unfortunately there has been no opportunity up to the present time to experiment with freshly gathered latex, which must be treated more delicately than is necessary with 38-40 per cent preserved latex, the only type which was available for the experiments. However, it seems fairly certain that fresh latex can be concentrated much more easily by the use of a high-frequency heating unit than by conventional methods. An indication of this is the fact that if ammoniacal latex is boiled in an ordinary receptacle, *e.g.*, a Pyrex beaker, a deposit of rubber soon forms on the hot walls, whereas if high-fre-

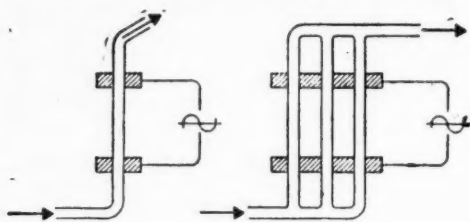


FIG. 4

quency heating is employed, the heat develops simultaneously and uniformly within the entire liquid mass, the boiling point is reached without trouble, and the liquid continues to boil without appreciable coagulation, either within the mass of liquid or on the walls of the receptacle.

This experiment was repeated with ammoniacal latex circulating continuously in a glass tube, and the results were just as satisfactory.

By using an apparatus in which a rectangular tank was supplied in such a way that the liquid was at a constant level at all times and air was blown

through it, it was found possible to reach concentrations higher than 70 per cent, and the quality of these highly concentrated latices was very satisfactory from all points of view.

In no case was any degrading effect of the electric field observed, and such an effect would seem unlikely to happen when it is considered how relatively inert are latex particles to various agents which have a degrading effect on dry rubber. Latex is, for example, less sensitive to ozone and hydrogen peroxide, and for this reason it is possible to manufacture sponge articles by coagulation of foamed latex, the swelling agent of which is oxygen liberated by decomposition of hydrogen peroxide which has been added to the mass. In spite of intimate contact of the hydrogen peroxide at the beginning and of oxygen subsequently with the rubber in emulsion, the aging of sponge articles made by this process is excellent. Furthermore it would be surprising if the high-frequency field were to have a depolymerizing effect on the latex particles because, when pure rubber is exposed to high-frequency electric fields, the changes which take place are the same as those which take place when it undergoes the corresponding thermal treatment. Radiothermal plasticization of solid masses of rubber yields products which retain their plasticity permanently and do not become sticky or brittle, even after several years of storage.

Similarly, rubber mixtures vulcanized by high-frequency electric fields age just as well in every way as do the corresponding mixtures vulcanized by conventional methods. This question of aging has arisen many times, but no experiments carried out by the present authors have given any indication of poorer quality because of radiovulcanization. It is in fact difficult to understand why radioheating should give products with any different properties from those obtained by ordinary methods of heating. The wave length which is used is extremely long compared to that of active luminous rays, *e.g.*, in most cases wave lengths of 15 to 20 meters have been employed, and even if it were necessary to change to wave lengths of only a few meters, which so far has not seemed to be of any advantage, these would still be far from the wave lengths of actinic rays.

Radioheating merely substitutes one means of molecular agitation for another. When a material is heated, the effect is fundamentally to increase the motion of the molecules, a thermal motion which is disordered in character. The use of a high-frequency field superposes a rhythmic motion on the thermal motion, but the amplitude of the mean movements should not increase, and only the manner of producing the molecular impacts is altered. If the application of short waves were to alter the structure or the aging properties of the products so treated, this should be particularly evident in processes of heating which involve infrared radiation, the wave lengths of which are far shorter than those of the wave lengths concerned in the present work. As far as any information available to the present authors is concerned, no effect of this kind has been reported, and it is necessary to drop down to wave lengths in the ultraviolet range to find any degrading action. It might be mentioned in passing that the use of ultraviolet radiation as a means of vulcanization has already been patented.

Attention should be called also to a special application of a high-frequency electric field, the production of so-called denatured latex. It is known that ammoniacal latex which has been heated to a certain temperature may become resistant to the action of certain reagents, *e.g.*, acids, which would bring about coagulation of the latex if it had not been heated in this way. The tendency

of this heated latex to coagulate is restored by the addition of a small proportion of the original latex which has not been heated.

Now the production of latex of this kind is not easy industrially, but the use of a high-frequency electric field would render the process extremely simple and rapid. The equipment already described for concentrating latex is perfectly adapted to the purpose, and with it, it should be possible to produce industrially a latex of a type which we shall choose to call "passive", to characterize it by its inertness to ordinary reagents, in the same way that the term passive iron is used to designate iron which is rendered resistant to dilute nitric acid by a previous brief immersion in concentrated nitric acid. Such latex would be expected to be of particular interest in cases where the material to be coated or impregnated is of such an acid character that it causes ordinary latex to coagulate. Bongrand has shown, for example, that to obtain good impregnation of cotton fibres, it is necessary to adjust the pH value of the latex so that it is the same as that of the fibre. This operation would certainly not be necessary with passive latex.

Provided that these latices were to keep well, it is possible to foresee various applications, for they ought to be more easily transportable than acid latices, which attack metal containers and require special methods of packing.

It would likewise be of interest to know how latex of this type would behave with certain compounding ingredients which bring about coagulation in ordinary latex. It would be interesting, for instance, to know whether carbon black, which reinforces crude rubber but has no such effect in mixtures prepared from ordinary latex, would show its valuable reinforcing properties in denatured latex mixtures.

It remains to examine the cost of concentrating latex by high-frequency electric currents. Measurements which the present authors have made in the course of numerous experiments, not only with latex but with various other liquids, show that, if efforts are made to synchronize the circuits properly, the efficiency, expressed as the ratio of the quantity of energy transformed into heat to the energy recorded by the meter reaches or even exceeds 50 per cent.

The efficiency is all the better because it is possible to use relatively long wave lengths, which are much more easily controlled than are short wave lengths. Under these conditions, synchronization of the circuits is particularly easy, and the various losses are thereby reduced greatly.

Because of lack of sufficient accurate data, it is difficult to compare the costs of concentrating latex by a high-frequency current and by evaporation; furthermore the cost of electric energy varies somewhat on the plantations. Nevertheless it seems fairly certain that, all things considered, the use of electric energy at high frequency for concentrating latex compares favorably with other methods.

THE COAGULATION OF LATEX *

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The mechanism of the coagulation of latex is a very brief chapter in most treatises on rubber. The theories are numerous and conflicting. The most widely accepted interpretation is one in which the destruction of the stabilization membrane is postulated. Recently, in Haiti, I made an electrophoretic study of latex involving the determination of mobility rates and isoelectric points. The timing of the migration of individual latex particles obviously necessitated the use of a microscope. This permitted constant observation of the globules, so that not only were their rate and direction of movement observed, but their aggregation as well.

When latex is put into a buffer mixture of a pH value at or near the isoelectric point of the latex, agglutination of the particles takes place. While observing this incipient coagulation of the latex, I was led to the conclusion that, though pH values of isoelectric points indicate a protein covering on latex particles, electrophoretic behavior points to a surface which is, in part, non-protein. The very feeble charge on *Cryptostegia* latex globules in comparison with the greater charge on *Castilloa* and the still greater charge on *Hevea* suggests that there is least protein on the *Cryptostegia* particles, and most on the *Hevea* particles. This deduction receives even better support from the complete dissimilarity in the mobility curves of *Cryptostegia* latex particles and the isolated serum proteins. That there is a nonprotein component of the particle surface is hardly to be doubted. I thought it very probable that this nonionizable component is hydrocarbon, the same which constitutes the core of the latex globule.

Direct observation of incipient coagulation also revealed that there is no loss of identity of the globules and no destruction of the stabilization membrane on initial agglutination.

The foregoing experimental findings and the deductions based thereon met with some opposition. The surface of latex particles is generally assumed to be of pure protein, the hydrocarbon presumably not entering into the composition of the stabilization membrane at all.

The expression "stabilization membrane", as commonly used in the chemistry of emulsions, denotes all forms of coating on the surface of the globules, from monomolecular to multimolecular layers. Monolayers may occur in living systems, but multilayers cover cells and natural emulsions. The stabilization membranes of some artificial emulsions may actually be isolated as delicate pellicles. Monolayers receive emphasis because they are more amenable to physical-chemical laws.

When latex particles collide, one of two events could take place, the particle may coalesce, as when two unprotected oil globules come into contact, or they may adhere and retain their identity. The former event occurs in a stabilized emulsion if, as a result of contact, the protective membranes break down. Through destruction of the membrane, the hydrocarbon in a latex globule is

* Reprinted from *Science*, Vol. 102, No. 2650, pages 378-380, October 12, 1945.

liberated and can then take part in coagulation, together with the protein components of the globule surface. If, however, the globules do not lose their identity and the original surface remains intact, then, when the globules collide and adhere, their stabilization membranes are alone responsible for the elastic qualities of the aggregate.

The evidence generally cited as proof that the stabilization membrane of Hevea latex is of protein and is destroyed on coagulation is the fact that latex film is irreversibly coagulated by dehydration, presumably because the protein is no longer an effective stabilizing agent. This is not very convincing proof. Isoelectric points established by electrophoretic studies¹ give better support to a protein covering on latex particles, for the isoelectric points are protein precipitation maxima. But these studies also give evidence of a nonprotein, nonionizable component in the surface layer of latex globules. I was reasonably content with this evidence, but as the research done in Haiti dealt primarily with electrophoretic behavior and the composition of the surface but not with coagulation *per se*, and not with the fate of the membrane, it seemed advisable to verify my interpretation of coagulation. Although there is no visible destruction of the stabilization membrane on coagulation and therefore no evidence that hydrocarbon takes part in coagulation, release of the hydrocarbon nevertheless is attributed to a breakdown of the surface. Doubting this, I again journeyed into the field, to the Government Agricultural Station at Coconut Grove, Florida, where the Director, Harold Loomis, placed the facilities of the station at my disposal, for which I here express my appreciation. Latices of the following plants were examined: *Cryptostegia grandiflora*, *C. magagascariensis*, the natural F₁ hybrid of the two foregoing species, *Ficus elastica*, *Hevea braziliensis*, *Manihot glaziovii*, *Funtumia elastica* and *Landolphia droogmansiana*.

The latices of the foregoing eight species of plants showed but slight differences in behavior, principally in isoelectric points. The general conclusions on coagulation are, therefore, applicable to all the species. Differences in behavior were often greater between the twig and trunk latex of the same plant than between different species. I shall, however, restrict my statements to two plants, Hevea and Cryptostegia.

The latices were placed in sodium acetate-acetic acid buffers, the pH ranging from 2 to 7. Isoelectric points of the different species varied between pH 3.5 and 4.6.

The first step in the coagulation of latex is the coming together of two globules. On further agglutination there is evidence of polarity, for the globules tend to join in chains (Figure 1a). Chain formation is greatly increased by stretching. The fibrous appearance of crude rubber in the coagulating vat is a microscopic picture of aggregates of the minute chains to be seen through the microscope.

Several microscopic fibrils or chains of agglutinated globules when grouped in parallel alignment form a microscopic aggregate which can be stretched by hand with the aid of needles. A single microscopic chain may also be stretched by a simple device. When a preparation containing latex at the isoelectric point is so mounted that numerous air bubbles are included, a single chain of latex globules may be found with one end attached to the surface of the glass slide and the other end held by tension to the surface of an air bubble. If now, the air bubble, by slight pressure is made to move to the edge of the slide, the chain of globules, which is actually a delicate strand of rubber, is stretched. This picture, when viewed under a magnification of 1350 \times , reveals

very clearly that it is the surface layer, the stabilization membrane, which is being stretched (Figure 1b). Moderate stretching leaves the globules still intact, with no destruction of the membrane. Repeated stretching, done on larger threads which are fascicles of single chains, reduces the size of the globules through incorporation of more and more hydrocarbon from the core of the globule into the surface complex (Figure 1c). Elasticity, that is to say, the degree of extensibility and rapidity of return, is very great. The globules, which are at first in direct contact, become more and more separated through repeated stretching (Figure 1, a, b, and c). The intervening substance composing the much stretched thread is crude rubber; it is the former surface layer of the globules which has increased in bulk at the expense of the inner hydrocarbon.

The original membrane, which on initial contact suffered no modification, has now, through repeated stretching, been so greatly modified that it has lost its identity as a surface covering (Figure 1c). To escape the rather incongruous situation of switching from a fiber which is initially elastic because of the protein composition of its surface to a later stage in the transformation of that fiber which is now elastic because of a protein-hydrocarbon complex, it is

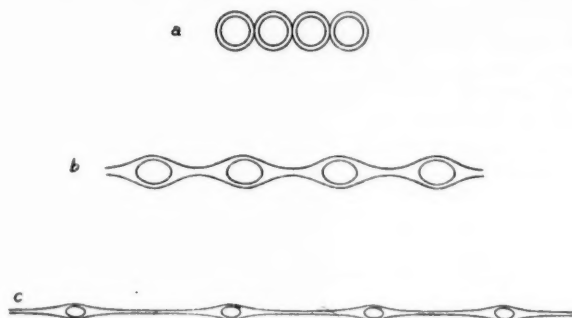


FIG. 1

only necessary to assume that hydrocarbon enters into the composition of the original membrane. The feeble zeta potential on *Cryptostegia* latex globules, and the dissimilarity between the migration curves of latex globules and serum proteins, give experimental support to this view.

The foregoing deduction is in keeping with much work on the chemical nature of the surfaces of living cells and natural emulsions. Biologists have long regarded cells as coated with fatty substances. Recently, the milk globule, heretofore thought to be stabilized by casein, has been shown by Palmer² and by Moyer³ to be a complex of phospholipids and protein. Moyer's work on milk is very similar, both as to method and the conclusion reached, to the study on latex reported here.

It is difficult to escape the conclusion that molecular continuity exists between the core and the surface of latex globules, and that the elasticity of crude rubber when first formed resides in a surface layer which is a composite of protein and hydrocarbon.

REFERENCES

- ¹ Seifriz, *India Rubber World* 112, 587, 729 (1945).
- ² Palmer, *J. Biol. Chem.* 104, 359 (1934).
- ³ Moyer, *J. Biol. Chem.* 133, 29 (1940).

RELATIONS BETWEEN THE QUALITY OF LATEX AND ITS CHEMICAL COMPOSITION *

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One of the chief technical difficulties when latex is used industrially for the manufacture of rubber articles is that there is no method available for determining whether or not successive shipments of latex are suitable for any particular process of manufacture. Two samples of latex may be similar in appearance and have nearly the same chemical properties with respect to dry rubber content, total solids and alkalinity, yet one sample may be in excellent condition, whereas the other sample is on the point of coagulating. When these two samples are mixed with compounding ingredients, one remains quite fluid, while the other thickens or even coagulates. Then again, when treated with a coagulant, one sample gels in a normal way and under conditions compatible with good processing, whereas the other sample gels either too rapidly or too slowly, or coagulates to an unusable mass. It is safe to say that there is no generally acceptable method with which it is possible to judge the quality of latex, and the different procedures which have been suggested cannot be regarded as satisfactory.

Rubber planters have called attention many times to the large variations in the properties of natural latex. Preserved latex is perhaps even more variable, for new factors then enter and influence its properties, *e.g.*, the effects of bacteria before any preservatives are added to the latex, and chemical reactions which take place between certain components of the latex and the preservatives. In addition, the properties of latex change continuously with age, which is extremely limited compared with that of dry rubber.

Table 1 gives some numerical data to show the changes which take place when ammonical latex is stored for periods as long as three years. The changes in dry rubber content and in alkalinity were insignificant. However, at the end of three years, some of the samples were in very bad condition; they had become very dark in color, and contained large proportions of coagulum, which made it difficult to determine the dry rubber content and alkalinity. These products were no longer in satisfactory condition for industrial use.

Very little is known about the nature of the changes which take place during a period of storage of three years. In any event, in the cases just described, the latices underwent far-reaching changes, and became absolutely useless. These changes could not be attributed to incomplete treatment of the latex originally because the latices which contained abnormally high percentages of ammonia deteriorated just as rapidly as those containing a normal percentage.

An estimation of the gradual deterioration which took place during storage of the various samples of latex was made by means of the stability test described by Davey and Coker¹. This method is purely empirical; nevertheless it was

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 18, No. 3, pages 90-93, May 1941.

TABLE I

Country of origin	Type of latex	Kind of container	Dry rubber content after				Ammonia (NH ₃) content after				Stability (no. of thousands of revolutions)			
			6 mo.	1 yr.	2 yrs.	3 yrs.	6 mo.	1 yr.	2 yrs.	3 yrs.	6 mo.	1 yr.	2 yrs.	3 yrs.
Malaya	Natural latex containing ammonia	tinplate	36.3	35.8	35.8	36.0	0.74	0.79	0.76	0.64	71	53	28	3 } slow speed 3 } 2 }
		tinplate	36.1	35.4	35.2	35.6	1.22	1.19	1.12	0.90	73	40	26	
		tinplate	36.2	35.6	35.4	25.3	1.62	1.58	1.52	1.53	65	41	24	
		tinplate	36.2	35.6	35.4	25.3	1.62	1.58	1.52	1.53	65	41	24	
Ceylon	Natural latex containing ammonia	glass	39.2	39.2	39.0	—	0.48	0.49	0.50	—	27	27	20	— } high speed — } — } — }
		tinplate	39.4	39.3	39.2	—	0.49	0.49	0.49	—	30	23	20	
		glass	39.9	39.8	39.5	—	0.82	0.80	0.81	—	29	25	13	
		tinplate	39.8	39.8	39.5	—	0.79	0.79	0.80	—	26	26	17	
Ceylon	Creamed latex	glass	52.7	52.8	52.7	—	0.42	0.42	0.43	—	21	23	20	— } high speed — } — } — }
		tinplate	52.7	52.7	52.6	—	0.43	0.41	0.41	—	20	21	20	
		glass	57.4	57.2	57.0	—	0.49	0.52	0.52	—	17	16	19	
		tinplate	57.3	57.3	57.3	—	0.49	0.48	0.49	—	15	13	14	

the best one available at the time these tests were started. The chief criticisms which can be made of the method are, on the one hand, that it does not correspond very closely to the conditions under which latex is used industrially and, on the other hand, that the order of stability of different latices depends to a great extent on the speed of stirring. In the method of Davey and Coker, this speed was fixed arbitrarily, but since that time it has been proved that some samples of latex are much more stable than others at high speeds of stirring, whereas the contrary is true at lower speeds of stirring.

The use of the term "stability test" in the sense above approaches technical practice. But this use creates a certain confusion, for the word stability designates not only resistance to coagulation but also resistance to changes in properties during storage. In other words, stability can be regarded either as a measure of the way in which a latex behaves in certain manufacturing operations at the particular time when the test is carried out, or as a measure of the length of time that a latex can be stored and still remain in satisfactory condition for processing.

It can be seen, for instance, from the data in Table 1 that, after six months, ordinary latex from Ceylon was more stable than creamed latex, insofar as it was more resistant to coagulation by zinc oxide. On the contrary, from the standpoint of the changes which it underwent during storage, the creamed latex was the more stable product. To avoid such confusion, the present author suggests the term *gelation test* for the determination, by some suitable method, of resistance to coagulation, and the term *storage test* for the determination of the changes in the properties of a latex on aging. The storage test need be merely successive gelation tests of samples at long intervals of time. A more important question is not whether a sample is more or less resistant to gelation, but whether or not this resistance changes rapidly during storage.

Even at the present time there is no satisfactory procedure for carrying out a gelation test. Nevertheless, experiments carried out with a series of samples of latex make it possible to offer some information on the subject. All the samples were prepared by the Rubber Research of Ceylon from the same original latex. Table 2 shows the differences in the four samples.

All the samples listed in Table 2 were prepared from the same original latex, and differed only in the dimensions of their particles, in their rubber content, and in their content of serum substances. The samples thus comprised a series with which it was possible to study the influence of these different factors in gelation tests. One of the samples (Sample E) contained a creaming agent capable of exercising considerable effect. Aside from this particular sample, all the others contained the same hydrocarbon and the same serum substances as those of the original latex, since in the centrifuging process it is possible to separate the serum substances to only a limited extent.

Each sample was diluted in such a way as to reduce its dry rubber content to 30 per cent; then a coagulation test was carried out by stirring with zinc oxide, calcium chloride, sodium fluosilicate or extremely finely divided silica. Under these conditions the concentration of serum substances differed greatly. It was also thought of interest to study the coagulation of undiluted samples in which the concentration of rubber differed considerably, but in which the concentration of serum substances was practically the same. In this way it was possible to determine separately the influence of the concentration of dry rubber and also of the concentration of serum solids on the tendency to coagulate. It was likewise possible to ascertain to what extent the dimensions of the particles have any effect on the resistance to coagulation.

TABLE 2

Sample	Method of preparation	Dry rubber content (percent-age)	Total solids (percent-age)	Ammonia (NH ₃) content (percent-age)	Notes
A	Original latex	37	40.3	0.66	Normal dispersion of latex particles
B	Centrifuged cream	60.2	62.3	0.56	Large particles in majority
D	Cream obtained from recentrifuged creamed latex	50.2	53.2	0.86	Particles of average size
E	Centrifuged latex creamed by addition by Tragon-A	35.5	39.4	0.87	Small particles

The experiments, the results of which are summarized in Table 3, make clear certain points.

(1) The samples can be arranged in approximately the same order with respect to their resistance to coagulation, whatever the testing method employed. However, the use of sodium fluosilicate is preferable to that of zinc oxide, silicate or calcium chloride, for with sodium fluosilicate coagulation takes place much more sharply, and the test can be carried out under conditions which approach closely the operating conditions prevailing in the industry.

(2) The higher the dry rubber content of a latex, the more readily does it coagulate.

(3) The size of the particles has no significant influence on the tendency of a latex to coagulate.

(4) The higher the concentration of serum substances in latex, the greater the resistance of the latex to coagulate. This is in accord with what is found in the practical test of rubbing purified latex or whole latex in the palm of one's hand.

In studying the relations between the chemical composition of latex and its quality, it is necessary to study separately the influence of the different phases of which latex is composed, *viz.*, the rubber phase, the aqueous phase of the serum, and the surface of separation of these two phases.

The tests which have already been described show that the tendency of latex to coagulate depends on the concentration of the rubber phase and on the concentration of nonrubber substances in the aqueous phase. In industrial practice, it is always possible to change at will the concentration of the rubber, but it is much more difficult to adjust the concentration of the serum substances to any desired value.

Finally, the third phase unquestionably plays an important part, yet the tests described above give no indication on this point. However, it has been possible to obtain some data on the part played by the boundary surface between the rubber particles and the aqueous phase by preparing serum absolutely free of rubber, and determining the concentration of the nonrubber substances in the aqueous phase and then in the whole latex. The difference between the two values represents the nonrubber substances which are not contained in the aqueous phase and which consequently are associated either with the rubber or are at the boundary surface of the rubber particles and serum. Table 4 gives the quantities of nitrogen bound to 100 grams of rubber and to 100 grams of aqueous serum for each of the four latices chosen for the tests.

TABLE 3
STABILITY OF LATEX
(Number of revolutions to bring about coagulation at 30° C)

Sample	High-speed stirring—50 cc. of latex					Slow-speed stirring—300 cc. of latex				
	Diluted to 30% 7.5 g. ZnO	Diluted to 30% 50 g. silica	Not diluted 7.5 g. ZnO	Diluted to 30% and 2% aqueous CaCl ₂ added			Diluted to 30% 1 g. Na ₂ SiF ₆	Not diluted 1 g. Na ₂ SiF ₆	Diluted to 30% 1 g. Na ₂ SiF ₆ , 0.6 g. NH ₃	Diluted to 30% 45 g. ZnO
				1 cc.	2.5 cc.	5 cc.				
A	23,900	22,200	19,700		16,300	6,100	5,600	4,300	2,800	46,340
B	8,280	9,000	3,100	15,800	1,200	300	2,200	9,200	4,200	5,260
D	8,100	14,000	12,200		6,900	700	4,000	16,700	7,300	7,100
E	29,900	59,300	34,800		11,700	5,300	6,700			{ 92,030
		{ 35,500								
										{ 90,710

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TABLE 4

Sample	Size of particles	Dry rubber content of latex (percentage)	Nitrogen in 100 grams of aqueous phase (grams)	Nitrogen associated with 100 grams of rubber (grams)
A	Normal distribution of particle size	24.7	0.184	0.153
B	Preponderantly large particles	25	0.082	0.133
D	Particles of average size	25.6	0.122	0.211
E	Small particles	24.8	0.230	0.289

These results show that the smaller the particles, the greater is the proportion of nitrogen associated with the rubber. This is what would be expected if it is considered that almost all of the nitrogen is present on the surface of the particles and that, for a given weight, small particles have a greater total surface area than large particles. That this nitrogen is located on the surface of the particles is confirmed by determinations of the distribution of the nitrogen, which show that all of the nitrogen (except 0.03 per cent based on the rubber phase) can be replaced by surface-active substances, such as potassium oleate or ammonium oleate; the nitrogeneous substances pass into the aqueous phase and part of the soap takes its place.

The results of the coagulation tests given in Table 1 show that there is no well defined relation between the quantity of nitrogen in the surface layer in the 100 grams of rubber and the resistance of the samples to coagulation. Nevertheless the concentration based on the actual surface area is not known, and the results of coagulation tests can be regarded as proof that the surface conditions are similar in the four samples originally prepared from the same latex and that, for a given sample of latex, the concentration of nonrubber substances in the boundary surface is almost the same for the large particles as for the small particles. Under these conditions, the values of coefficient N_r , given in Table 4, for these different samples can be regarded as a rough indication of the relative sizes of the particles when size is defined as the ratio of total volume to total surface. On the contrary, when applied to samples obtained from different latices, N_r values cannot be utilized to compare the sizes of the particles in samples of this kind.

The fact that the surface concentration of the nonrubber substances is not appreciably influenced by the size of the particles is confirmed by the results of experiments in which samples were spread out as a monoglobular layer on the surface of an aqueous solution in a Langmuir-Adam tray, and compressing the layer until all the particles were in contact with one another. The area occupied is directly proportional to their surface area, and the relative sizes of the particles determined by this method are in satisfactory agreement with the values calculated with the aid of the N_r values. It is evident, therefore, that the four samples examined did not differ much as far as the boundary surface of the particles and serum is concerned, and therefore that it is of little value to examine this phase in attempts to judge the quality of a latex. On the other hand, the study of these samples shows how very important it is to examine the serum phase. The results of such an examination are summarized in Table 5, in which the numerical values are expressed in terms of the percentage of the values obtained when working with centrifuged cream.

To obtain more precise data on the manner in which the boundary phase influences the resistance of latex to coagulation, it is necessary to apply other methods.

Attention has already been called to the importance of certain surface-active substances, such as potassium oleate, which are capable of replacing proteins on the surface of rubber globules. It is known that "whole" latex

contains approximately 1 per cent (based on the rubber) of higher fat acids, which are probably present in the form of ammonium soaps. It has likewise been proved that the proportion of these fat acids fluctuates in practice over rather wide limits². Now the acid number of latex has a tendency to increase during storage, and since ammonium soaps are capable of replacing proteins on the surface of the rubber globules, any changes in the properties of latex which take place during storage can probably be attributed to the properties no longer depending on a surface layer of proteins but on a surface layer of soaps.

TABLE 5

Sample	Ratio of the N_r values (Table 4)	Ratio of the N_r values (Table 4)	Relative amounts of serum substances (difference between total solids and dry rubber)	Ratio of the number of revolutions to bring about coagulation with		Percentage with relation to the time of gelation of the latex with sodium fluosilicate	Relative pressure for a given surface concentration of rubber in a Langmuir-Adam tray
				sodium fluosilicate	zinc oxide		
A	1.15	2.26	2.3	2.5		2.8	2.3
B	1	1	1	1		1	1
C	1.6	1.5	1.7	1.8		1.6	1.8
D	1.1	2.8	2.8	3.1		3.1	3.5

But in spite of all this, even latices which have aged still contain appreciable quantities of nitrogenous substances on the surface of their globules. It has been observed that in 40 per cent latex twelve months old, and examined in London, the quantity of proteins on the surface of the rubber particles was approximately 1 per cent (based on the weight of rubber) compared to approximately 0.75 per cent of soaps. However, as a result of orientation, the surface area covered by proteins is several times greater than the surface area covered by soaps³. Consequently, the properties of even very old latex evidently depend chiefly on the proteins. Furthermore, evidence put forward by Rhodes that there is a definite correlation between the acid number of a latex and its resistance to coagulation by zinc oxide⁴ is of considerable interest in this connection.

The foregoing discussion seems to indicate that there are at least two chemical factors which play a part in the quality of any particular sample of latex, (1) the nature and concentration of the serum solids in the aqueous phase and, (2) the relative proportions of proteins and of soap in the boundary phase. The properties of latex are very sensitive to changes in these factors, but it is still too early to lay down any principles regarding their technical significance. Nevertheless, these preliminary findings should be useful as a starting point for new investigations having as their objective a better knowledge of the quality of latex and the improvement of its quality.

ACKNOWLEDGMENT

The author wishes to express his thanks to all his colleagues as well as to the Directors of the London Advisory Committee for Rubber Research in Ceylon and Malaya, who gave permission for him to make use in the present communication of the results of the experimental work.

REFERENCES

- ¹ Davey and Coker, *Trans. Inst. Rubber Ind.* 13, 368 (1938); *RUBBER CHEM. TECH.* 11, 459 (1938).
- ² Rhodes, *J. Rubber Research Inst. Malaya* 9, 134 (1938), Communication No. 238.
- ³ Adam, "The Physics and Chemistry of Surfaces," 1939, p. 89.
- ⁴ Rhodes, *J. Rubber Research Inst. Malaya* 9, 137 (1938), Communication No. 238.

DIFFERENTIATION OF RUBBER AND GUTTA HYDROCARBONS IN PLANT MATERIALS *

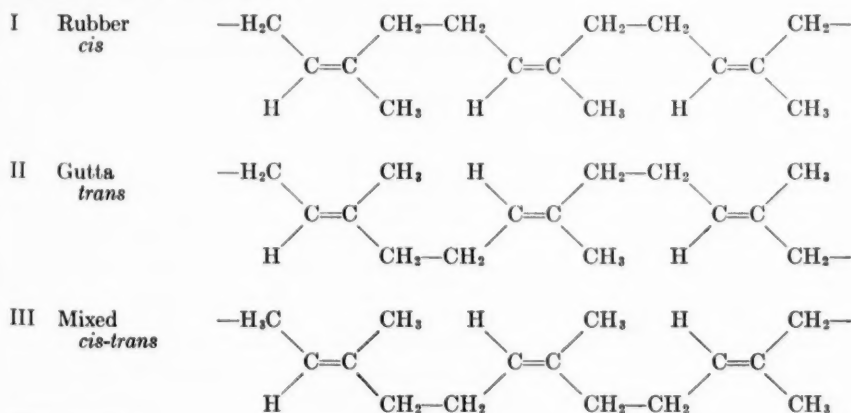
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INTRODUCTION

The isomeric hydrocarbons, gutta and rubber, are obtained commercially from only a few plants. They occur, however, in amounts varying from traces to major components in many plants, and it has been an objective of this Bureau to evaluate such sources. In several instances, the isolated hydrocarbons could not be definitely identified by their elastic properties, which were intermediate between rubber and gutta. Thomas A. Edison, whose notes are on file in the Office of Rubber Plant Investigations, also experienced this difficulty. He examined some 17,000 plant samples comprising more than 1000 genera in his search for a native source of rubber. Using solvent extraction, Edison often isolated a polymerized hydrocarbon which he was unable to designate as being either rubber or gutta. Work reported here was undertaken to clarify this matter and to provide an initial approach to the biochemical problem in the manner in which such polymers are made by plants.

Rubber and gutta have the same empirical formula, $(C_5H_8)_x$, but differ in the spatial positions of their carbon atoms about the double bonds, as shown by Formulas I and II, rubber being the *cis*- and gutta the *trans*-isomer for chain continuation¹. It was felt that the intermediate elasticity of some samples might be the result of a simple mixture of rubber and gutta or due to the presence of a "mixed" molecule in which both the *cis*- and *trans*- forms might appear (Formula III).



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Chemical reactions are of little value in the identification of the isomers, since the same end products are obtained when the double bonds, the only reactive parts of the molecules, are destroyed. Absorption of light and solubility behavior in hydrocarbon solvents are more promising methods for differentiating the compounds. Rubber and gutta absorb light only in the infrared and far ultraviolet regions of the spectrum. In the ultraviolet, where light absorption is determined by electronic transitions, significant differences are not to be expected. In the infrared, however, differences between rubber and gutta occur, since light absorption is a result of vibrations of all the atoms in a molecule. These vibrations are to a great extent independent of the number of repeated units in a polymerized material, but are influenced by the type of isomerization within a unit.

EXPERIMENTAL

INFRARED ABSORPTION

Infrared transmission measurements were made with a nonrecording spectrograph located at the Palmer Physical Laboratory of Princeton University, for the use of which we are indebted to Professors L. G. Smith and Walker Bleakney. The spectrograph is of the rock salt prism type and utilizes a thermopile for the detection of radiation. The thermopile is connected in series with a sensitive galvanometer from the mirror of which light is reflected into a photoelectric amplifier which operates a second galvanometer. Transmitted energy is proportional to the deflection of this second galvanometer. A "globalar" rod heated by alternating current is used as a source of radiation. On account of the spectral energy distribution from the source, it is necessary to increase the slit widths as the wave length increases. Such adjustments were made at selected points along the wave-length scale.

Films for transmission measurements were made by placing several drops of a 2 per cent hydrocarbon solution in a volatile solvent on a carefully polished rock salt plate (1.5×5 cm.). After evaporation of the solvent, the process was repeated two or three times until a uniform film of the order of 0.02 mm. in thickness was obtained. The plate and its adhering film were placed in a holder arranged to be introduced into the light path of the spectrograph.

Transmission values, T , were obtained at intervals of 0.05 to 0.15 μ from measurements of the fraction of light transmitted by the film. These values were reduced to corresponding opacities, K , by use of the equations:

$$I_t + I_0 10^{-K}, \text{ or } -\log \frac{I_t}{I_0} = -\log T = K$$

in which I_0 is the incident energy (initial galvanometer deflection) and I_t is the transmitted energy (galvanometer deflection with the film in the light path). The opacity, K , is equal to the product of the linear absorption coefficient, a , and the thickness, t ; i.e., $K = at$. Calculation of opacities is only physically significant for films of uniform thickness and absolute absorption coefficients cannot be calculated unless the film thickness is known. An effort was made to obtain uniform films, and repetition of measurements on balata gutta and Hevea rubber indicated that uniformity in thickness was adequately attained. Absorption coefficients, a , of various samples can best be compared since they are independent of thickness, t , and combine linearly instead of logarithmically as do the transmissions. Accordingly, all absorption coefficients were reduced to the same relative scale as obtained from a sample of purified Hevea rubber.

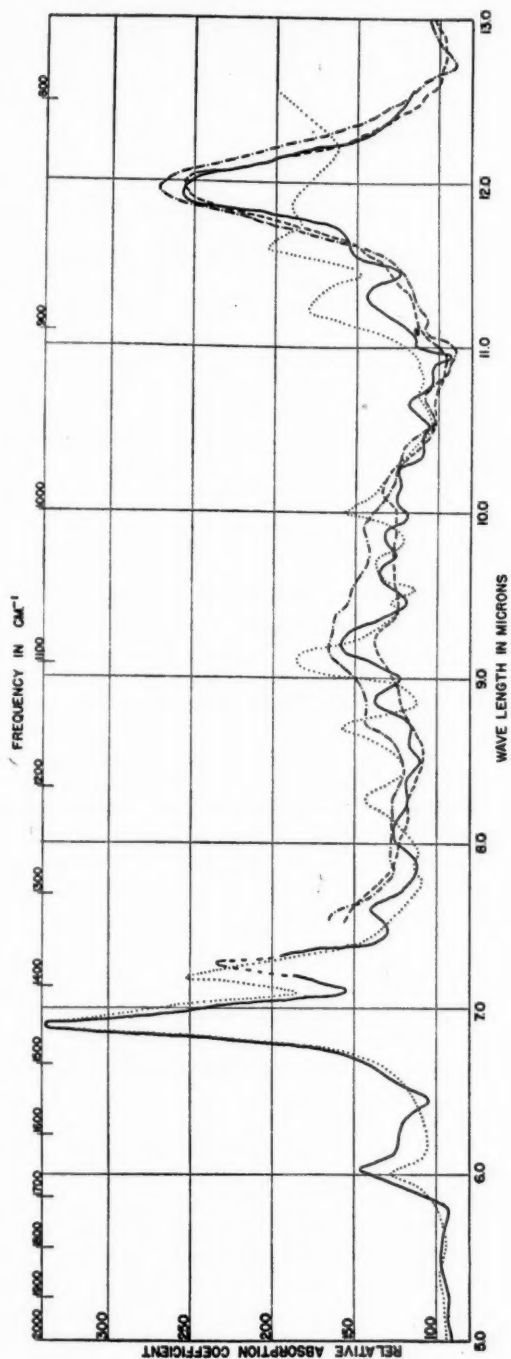


FIG. 1.—Infrared absorption spectra of hydrocarbons from *Hevea brasiliensis* (rubber —), *Mimusops balata* (gutta ····), *Solidago leavenworthii* (Goldenrod — — —), *Jatropha* sp. (Chilte — · — ·).

This was done for gutta by proportionate displacement along the ordinates (relative opacities) until the curve, Figure 1, was brought into general juxtaposition with that of Hevea rubber. Where measurements were made only in the region of $12.0\ \mu$, opacities and therefore absorption coefficients were reduced to the same relative scale by adjusting them to agree with curves for rubber and gutta at $12.25\ \mu$, that is, where the curves cross.

PREPARATION OF HYDROCARBONS AND INFRARED MEASUREMENTS

Rubber obtained from *Hevea brasiliensis* latex was used as a polymerized hydrocarbon having the *cis*-configuration. Nonrubber components were removed by anaerobic bacterial action. The dried coagulum was dispersed in benzene and precipitated with acetone. Repeating this process four times produced a material nearly colorless in benzene solution. Balata gutta (*Mimusops balata*) was used as representative of a *trans*-compound. A sheet of balata was extracted with hot water, the hydrocarbon dispersed into benzene, centrifuged, and the hydrocarbon precipitated from the clear centrifugate with an equal volume of acetone. The precipitated gutta was washed with acetone and twice recrystallized from petroleum ether.

Spectrographic results obtained from these two hydrocarbons are shown in Figure 1. A significant difference in absorption coefficients occurs in the region 11.8 to $12.3\ \mu$, where, at $12.0\ \mu$, the relative absorption coefficients of rubber is 42 per cent greater than for gutta². These measurements and the ones for gutta are in close agreement with those of Stair and Coblenz³, which are the only other ones previously reported. Two other samples of purified crepe Hevea rubber gave essentially the same results in the region of 11.3 to $12.5\ \mu$, the only region measured. Therefore, a clear-cut method is offered for differentiating between rubber and gutta, and hence between *cis*- and *trans*-isomerisms in rubber hydrocarbons involving intra- or intermolecular mixtures.

Absorption measurements in the region of 11.0 to $13.0\ \mu$ of prepared mixtures of gutta and rubber containing 10, 20, and 40 per cent rubber, respectively, showed that less than 10 per cent of rubber could readily be detected. One of the samples of gutta used in this work showed considerably greater absorption in the region of $11.24\ \mu$ than did the standard sample. This absorption is probably due to oxidation, which is the first step toward the more seriously degraded material studied by Stair and Coblenz³ (their old rubber).

Two species of milkweed were examined. *Asclepias erosa* latex obtained from Arizona was evaporated to dryness and exhaustively extracted, first with acetone and then with benzene. The hydrocarbon in the benzene solution was precipitated with acetone, dried, dissolved in carbon tetrachloride, and used for spectrographic analysis. *A. syriaca* was collected locally and the hydrocarbon prepared in the same manner as for *A. erosa*. Both hydrocarbons were considerably less elastic than benzene-extracted Hevea rubber. Figure 2 shows, however, that both compounds have the same absorption coefficients as rubber in the region 11.3 to $12.5\ \mu$.

The hydrocarbon of evening primrose (*Oenothera biennis*) was extracted from dried leaves with benzene after thorough acetone extraction. It was recovered by evaporating the benzene solution to dryness. Absorption coefficients relative to Hevea rubber are shown in Figure 3. This plant, like the milkweeds, appears to make rubber to the exclusion of gutta.

A sample of goldenrod (*Solidago leavenworthii*) hydrocarbon, obtained through the courtesy of the Southern Regional Research Laboratory of the

Bureau of Agricultural and Industrial Chemistry in New Orleans, was examined. The hydrocarbon was precipitated from a 10 per cent solution in benzene by addition of ethanol. It was dissolved twice in benzene and reprecipitated with acetone. The final product was exceedingly sticky and had only a very slight amount of elasticity. Yet, as Figure 1 shows, the absorption coefficients are nearly the same as those found for Hevea rubber, and this compound must be considered to have the *cis*-configuration.

An opaque and rather inelastic sample of chilte rubber (*Jatropha* sp.) was dissolved in benzene, centrifuged, and the hydrocarbon thrown out of solution by addition of acetone. The sample was then swelled in petroleum ether and a very small residue (about 1 per cent) removed by centrifuging. The petroleum ether solution was used for preparing films. Relative absorption

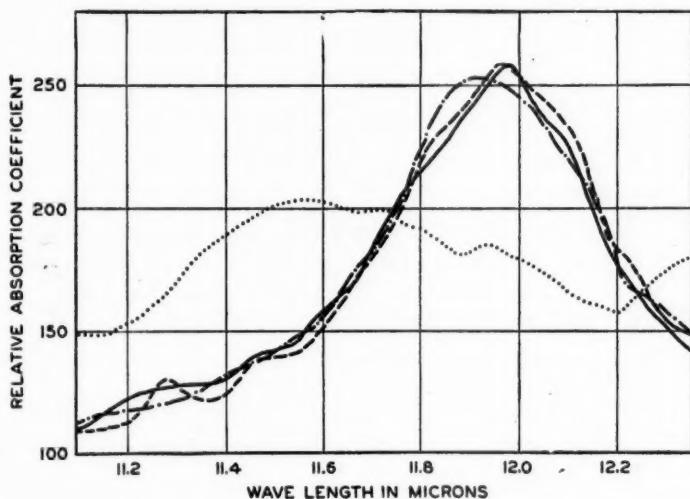


Fig. 2.—Infrared absorption spectra in the region of 12 μ of hydrocarbons from the milkweeds, *Asclepias erosa* (— — —) and *Asclepias syriaca* (— · — · —) compared with rubber (—) and gutta (· · · ·).

coefficients, as shown in Figure 1, agree closely with those of rubber, and there can be but little doubt that the hydrocarbon has the *cis*-configuration. The reduced elasticity is probably associated with the large amount of resinous substances found in the rubber.

There has been some doubt about the nature of the hydrocarbon obtained from *Eucommia ulmoides*. After extraction of a large amount of locally procured bark, first with acetone and then with benzene, the hydrocarbon regained from benzene was treated in the same manner as described for balata gutta. The final product had the appearance of an excellent grade gutta percha. In Figure 3, the good agreement between relative absorption coefficients for *Eucommia* hydrocarbon and gutta from balata is illustrated. The agreement is close except in the region of 11.5 μ , where there is a small deviation which is probably due to some oxidation. Whether this difference is reflected in the considerably higher melting point of *Eucommia* gutta (78°C) compared to balata (58°C) is not known. The infrared spectra, however, show that both of these compounds have the *trans*-type of isomerism in spite of some differ-

ences in physical properties. *Eucommia* is being exploited in Russia as a source of high-grade gutta⁴.

On several different occasions, Edison examined *Euonymus japonicus* without being able to decide whether the hydrocarbon he obtained was rubber or gutta. To clarify this matter, leaves collected locally were dried and powdered, and then extracted with acetone and benzene. The hydrocarbon, precipitated by addition of acetone to the benzene solution, was redissolved in benzene and fractionally precipitated with acetone. The final three-quarters of the material was retained for experimentation. Examination of Figure 3 shows that the absorption coefficients of this hydrocarbon agree within limits of experimental error with those of gutta from balata and *Eucommia*. Other species of *Euonymus* are being utilized as sources of gutta in the Soviet Union⁴.

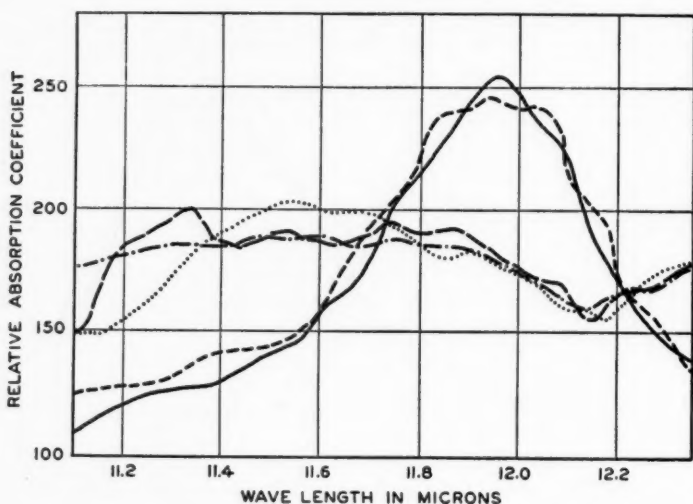


FIG. 3.—Infrared absorption spectra in the region of $12\ \mu$ of hydrocarbons from *Eucommia ulmoides* (—), *Euonymus japonica* (— · — · —) and *Oenothera biennis* (Evening Primrose — — — —) compared with rubber (—) and gutta (· · · · ·).

SOLUBILITY EXPERIMENTS ON RUBBER-GUTTA MIXTURES

Previous work on the solubility of rubber and gutta in petroleum ether suggested the possibility of using this solvent to effect their quantitative separation. Sol rubber readily dissolves and gel rubber swells in petroleum ether. Gutta, on the other hand, can be recrystallized from petroleum ether.

Hevea rubber in the form of smoked para sheet was allowed to swell for 7 days in petroleum ether, after which the mixture was centrifuged and the resulting clear solution of sol rubber retained for further use. Balata gutta, purified as described previously, was dissolved in hot petroleum ether and then added in various proportions to fractions of the sol-rubber solution. The rubber-gutta solutions were then cooled to -8°C , and examined after 30 minutes for evidence of crystallization. Gutta separated quantitatively, with greater than 98 per cent regain, from a solution in which it was present in $\frac{1}{4}$ the concentration of sol rubber. It was also observed to separate at 0.04 and 0.02 concentrations relative to rubber in approximately 2 per cent rubber solutions.

Because of its opaqueness and reduced elasticity compared to Hevea rubber, chilte hydrocarbon was examined for a possible gutta fraction by solubility behavior in petroleum ether. No material separated from 1.0 to 2.0 per cent solutions held at -8°C for 2 hours. Gutta which was added readily separated in $1\frac{1}{2}$ hours at -8°C from 1.0 per cent chilte rubber solutions in petroleum ether in which the concentrations of added gutta were 0.50, 0.25, 0.10, 0.05, 0.02, and 0.01 of that of the rubber hydrocarbon. It would appear from these experiments and infrared measurements that chilte rubber could not contain more than 1.0 per cent gutta, if any. Insolubility of gutta in cold petroleum ether, even in the presence of rubber, thus appears to offer a ready method for its preliminary identification.

The great difference in solubilities of rubber and gutta in petroleum ether is indeed noteworthy, considering their closely similar compositions. In view of this, it was of further interest to examine the solubility of gutta in rubber in the absence of solvent. Films were prepared by evaporation of rubber dissolved in benzene to which various amounts of gutta had been added. Separation of gutta in the dried films was readily detected by the presence of birefringent material in the unstretched films, using a petrographic microscope. Films containing 25, 50, and 75 per cent gutta were translucent, markedly less elastic than rubber, and highly birefringent. A film containing as little as 1 per cent gutta was noticeably birefringent, although its plastic properties were not obviously different from those of rubber.

Measurements of refractive indices and densities on films of rubber, and rubber-gutta mixtures gave further information that gutta is not mixed with chilte and goldenrod rubber. Values of these constants at 25°C are:

	Density	Index of refraction, n_D	Reference
Rubber	0.906	1.5190	(5)
Gutta	0.961	1.557	(6)

The density and refractive index of a substance are related by the Lorentz-Lorenz expression: $(n_D^2 - 1)/(n_D^2 + 2) = K_a\rho$, where K_a is a constant characteristic of the material and is equal to the molecular refractivity divided by the molecular weight. To a close approximation, the K_a values of rubber and gutta are equal, since their molar refractivities and molecular weights are both multiples of a C_5H_8 unit. In the first approximation, the refractive index of a rubber-gutta film in which the gutta is immiscible will depend linearly on the composition. Thus, 1 per cent of immiscible gutta should raise the refractive index of a film to 1.5194.

The refractive index was determined with an Abbé Zeiss refractometer used as a total reflectometer⁷. Densities were measured for small portions of the films by determining the density of an acetone-water solution in which they remained suspended. The results shown below clearly support the previous evidence for the insolubility of gutta in rubber and its absence in chilte and goldenrod rubber.

Substance	Density	Observed n_D at 25°C	Calculated n_D
50% rubber—50% gutta	—	1.531	1.538
75% rubber—25% gutta	—	1.527	1.528
Chilte rubber	0.909	1.519	—
Goldenrod rubber	0.906	1.519	—

DISCUSSION

Hydrocarbons isolated from the various plants were all definitely of the rubber or gutta types without evidence of inter- or intramolecular mixing. Physical properties of hydrocarbons (rubber = r, gutta = g) from many other species of plants of the *Asclepiadaceae* (r), *Apocynaceae* (r, g), *Moraceae* (r), *Euphorbiaceae* (r), *Compositae* (r), *Celastraceae* (g), *Sapotaceae* (g), and other families, leaves but little doubt that rubber or gutta alone generally is made in the plants. A specific plant would appear to have an enzyme or enzymes necessary for the linear condensation of a hydrocarbon polymer precursor exclusively in the *cis*- or in the *trans*-configuration, even though both are unstable with respect to an intramolecular equilibrium mixture. This is, of course, the condition generally found for both geometrical and optical isomers in living systems.

The ratio (x) of *cis*- to *trans*-forms at equilibrium is given by:

$$x = \exp (-\Delta F^\circ/RT')$$

where ΔF° is the standard free energy difference between the two forms. This ratio is unknown for a rubber-gutta mixture, but it can be estimated from two independent reactions in which similar groups are involved. One of these is the isomerization of oleic to elaidic acid for which the equilibrium mixture at 170°C in the absence of solvents contains about 20 per cent oleic acid⁸. The corresponding value of ΔF° is 1200 calories per mole. Similarly, the difference in the heats of bromination for *cis*- and *trans*-2-butene⁹ in the gas phase at 30°C is about 1000 calories per mole and the entropy difference between the two forms is probably small. Values for x and the percentage of the *cis*-form at equilibrium for various values of ΔF° are given in the following table (temperature = 300° abs.).

ΔF° (cal./gram molecular weight)	$x = \frac{\text{conc. cis-form}}{\text{conc. trans-form}}$	% <i>cis</i> = $\left(\frac{x}{1+x} \right) 100$
0	1.000	50
600	0.368	27
1200	0.135	12
1800	0.050	4.8
2400	0.018	1.8
6000	0.000045	0.0045

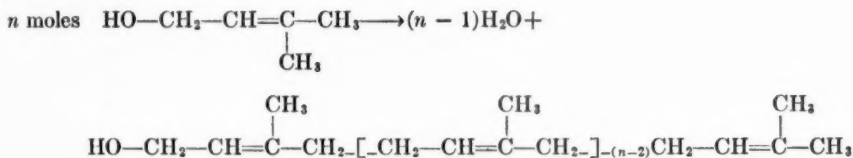
A rubber-gutta mixture thus should contain 10 to 25 per cent of the *cis*- or rubberlike configuration at equilibrium.

Two experimental methods were used in attempts to establish equilibrium between the *cis*- and *trans*-forms. The first of these made use of iodine as a possible catalyst for the isomerization of rubber to the equilibrium mixture. It failed, apparently because of loss of unsaturation due to cross-linking between groups. The second method depended on equilibrium being produced, at the time of formation, about the double bonds in commercial synthetic polyisoprene. This material might involve polymerization of isoprene elements through either end of the isoprene molecule. Cross-linking between groups had also occurred in the sample examined, which swelled rather than dissolved in benzene. Films made from the small amounts that dissolved in benzene gave infrared absorptions that were generally similar to rubber and gutta, but which were modified as expected for oxidized materials.

Rubber and gutta probably utilize the same precursor, and the only depar-

ture in their biosynthesis might be in the reaction which introduces or preserves the double bond of the polymerizing unit. Dehydrogenation after polymerization seems unlikely, since the chance would exist for failure of the reaction to be completely carried out, resulting in reduced unsaturation of the final product. Rubber and gutta have the same empirical formula, $(C_5H_8)_n$, and appear to contain one double bond to each unit within less than one part in a thousand¹⁰. If the isomerization is introduced before polymerization, at least two distinctly different enzyme systems would be required, one to differentiate the formation of the *cis*- or *trans*-precursor and the other to join the resulting *cis*- or *trans* form into linear polymers.

Polymerization of a precursor to form rubber or gutta is rather similar to the polymerization of glucose by α - or β -glycosidic linkages to form starch or cellulose. While both starch and cellulose are generally present in a plant, a mixed condensation of glucose by α and β linkages has not been observed. A probable situation in the case of rubber and gutta is that isomerism is introduced into the hydrocarbon molecule at the time of polymerization of the five carbon precursor. These conditions can be fulfilled by a reaction of the following type:



SUMMARY

Hydrocarbons of the rubber (r) or gutta (g) types isolated from *Hevea brasiliensis* (r), *Mimusops balata* (g), *Asclepias erosa* (milkweed (r)), *A. syriaca* (milkweed (r)), *Oenothera biennis* (Evening primrose (r)), *Solidago leavenworthii* (goldenrod (r)), *Eucommia ulmoides* (g), *Euonymus japonicus* (g), and *Jatropha* sp. (chilte (r)) were positively identified by their light absorptions near 12 μ . Mixed *cis*- and *trans*-isomers were absent in all cases, even though the plants examined were selected as giving hydrocarbon polymers of questionable types.

REFERENCES

- ¹ Mark, "Physical Chemistry of High Polymeric Substances", New York, 1940.
- ² Williams and Dale, *J. Applied Physics* **15**, 585 (1944).
- ³ Stair and Coblenz, *J. Research Natl. Bur. Standards* **15**, 295 (1935).
- ⁴ "Biochemistry of Cultivated Plants". Editor N. N. Ivanoff (Russian), Vol. IV. Inst. of Plant Industry, Leningrad, 1938.
- ⁵ Wood, Proc. Rubber Tech. Conf. London, 1938, pp. 933-953.
- ⁶ Kemp, RUBBER CHEM. TECH. **12**, 470 (1939).
- ⁷ McPherson and Cummings, *J. Research Natl. Bur. Standards* **14**, 553 (1935).
- ⁸ Griffiths and Hilditch, *J. Chem. Soc.*, 1932, 2315.
- ⁹ Conn, Kistiakowsky and Smith, *J. Am. Chem. Soc.* **60**, 2764 (1938).
- ¹⁰ Scheibe and Pummerer, *Ber.* **60**, 2163 (1927). Note also Bateman and Koch, *J. Chem. Soc.*, 1944, 600.